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SUFFIELD REPORT

NO. 488

IDENTIFICATION OF MUSTARD RELATED COMPOUNDS IN AQUEOUS SAMPLES BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY (U)

by

P.A. D'Agostino, L.R. Provost, A.S. Hansen and
G.A. Luoma (Defence Research Establishment Pacific)

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ABSTRACT

Thiodiglycol and a number of other compounds were detected during gas chromatographic analysis of aqueous samples obtained from near the site of the former DRES mustard hydrolysate vaults. Hexane extracts of the aqueous samples were analysed by capillary column gas chromatography-mass spectrometry (GC-MS) under both electron impact and chemical ionization conditions. Interpretation of the MS and complementary capillary column GC-fourier transform infrared data led to the characterization and identification of many compounds, including ether/thioether macrocycles and vinyl alcohol compounds, not previously associated with mustard decomposition.

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INTRODUCTION

1. During World War II over 700 tons of the chemical warfare agent mustard were shipped to the Defence Research Establishment Suffield (DRES) and stored in lead-lined concrete vaults (1). In the early 1970's it was decided that this stockpile of mustard would be destroyed by hydrolysis. Batch hydrolysis using 1000 gallons of mustard, 5000 pounds of lime ($Ca(OH)_2$) and 2500 gallons of water was carried out according to a method developed at DRES (2, 3).

2. The principle reactions involved in the hydrolysis of mustard (H) are shown in the equations below (4). Conversion of mustard, $\underset{\sim}{1}$, through hemisulfur mustard, $\underset{\sim}{2}$, to thiodiglycol, $\underset{\sim}{3}$, was essentially complete provided the ratio of water to mustard was large, the temperature was elevated to 100°C and the pH was maintained above 7 (3).

$$\underset{\underset{\sim}{1}}{Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + H_2O \rightarrow \underset{\underset{\sim}{2}}{HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + HCl$$

$$\underset{\underset{\sim}{2}}{HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + H_2O \rightarrow \underset{\underset{\sim}{3}}{HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}OH} + HCl$$

$$Ca(OH)_2 + 2\,HCl \rightarrow Ca(Cl)_2 + 2\,H_2O$$

3. Following batch hydrolysis the mustard hydrolysate was transferred from the reaction vessel into one of five empty storage vaults. After a cooling and settling period the hydrolysate separated into two layers. The upper or liquid layer was very fluid and ranged from clear to pale yellow in colour. The lower or sludge layer was paste-like and yellow-brown in colour. Samples of the liquid and sludge layers from the vaults, containing the mustard hydrolysate, were analysed for thiodiglycol, mustard and other organic content. Thiodiglycol was found in the 2 to 10 mg/mL range in the liquid hydrolysate and in the 6 to 14 mg/g range in the sludge hydrolysate (5). Mustard was found at trace levels in two sludge samples (5) and a number of other sulfur containing compounds were identified in extracts of the sludge and liquid hydrolysate samples (6).

4. Although the majority of the mustard hydrolysate was removed from the vaults, a residual amount remained. The residual hydrolysate was contained and encased with the remains of the vault after mustard destruction. Monitoring wells were established near this site to enable future sampling. This report summarizes the analytical findings of aqueous samples obtained from these locations.

5. Analysis of the aqueous samples by a previously described method (5) indicated the presence of thiodiglycol and several related compounds, including 1-oxa-4-thiane and 1,4-dithiane. Mustard was not detected in any of the samples. Hexane extracts of the aqueous samples were analysed under electron impact, isobutane CI and ammonia CI conditions in an effort to identify other aqueous sample components. Isobutane CI, a

technique recently applied to the analysis of mustard formulations (7, 8), was particularly useful as this method provided molecular ion and CI fragmentation ion information for all sample components. Interpretation of the EI and CI mass spectra, and data acquired during capillary column GC-fourier transform infrared spectroscopy (FTIR), led to the characterization and identification of many compounds including ether/thioether macrocycles and vinyl alcohol compounds, not previously associated with mustard decomposition.

EXPERIMENTAL

Aqueous Samples

6. Aqueous samples were taken in December 1984, March 1986 and March 1987 from the sampling locations established during encasement of the DRES mustard hydrolysate vaults. Samples were identified by year and sampling location (e.g., 84 – 5: March 1984/site # 5). Exact site locations have been reported internally at DRES.

7. Analysis of aqueous samples for thiodiglycol required no sample work-up. The other sample components were identified after extraction of 25 mL of aqueous sample with 3 × 5 mL hexane and concentration by nitrogen blowdown to approximately 1 mL.

Standards

8. "HPLC grade" hexane was purchased from BDH Company (Edmonton, Alberta). Thiodiglycol was purchased from Pierce Chemical Company (Rockford, Illinois). Purified mustard was provided by the Organic Chemistry Laboratory at DRES.

Synthesis of (2-Vinylthiol)ethanol

9. (2-Vinylthiol)ethanol, the first in a series of vinyl alcohol sample components, was synthesized according to the method of Nosyreva *et al* (9). Sodium sulfide (12 g) dissolved in water (25 mL) was thoroughly mixed with 2-chloroethanol (4 g) in dimethyl sulfoxide (25 mL). The reaction mixture was warmed to 65° C and acetylene was bubbled through the mixture for 6 hours. The product was allowed to stand overnight prior to extraction with dichloromethane (3 × 25 mL; dried over anhydrous sodium sulfate).

Removal of the dichloromethane *in vacuo* gave 2 mL of very pale yellow liquid. Partial purification in a Kugelrohr oven afforded 1.5 mL of colourless liquid containing approximately 30% (2-vinylthio)ethanol and 70% dimethylsulfoxide.

Instrumental Analysis

10. Thiodiglycol was determined by external standard calibration using a previously described method (5). Analyses were performed using a 1.22 m × 1.5 mm ID Tenax GC (60/80 mesh) column with the following temperature program: 150°C (2 min), 10°C/min to 250°C (10 min).

11. Hexane extracts of aqueous samples were analysed by capillary column GC-FID using 15 m × 0.32 mm ID J+W DB-5 and DB-1701 columns and the following temperature program: 50°C (2 min) 10°C/min 280°C (10 min). An on-column injector of our own design was used for sample introduction (10).

12. GC-MS analyses were performed with a VG 70/70E mass spectrometer equipped with a Varian 3700 gas chromatograph. GC-FTIR analyses were performed at Defence Research Establishment Pacific on a Nicolet 6000 GC-FTIR instrument equipped with a Hewlett Packard 5790 gas chromatograph. Table I lists the operating conditions used during GC-MS and GC-FTIR analyses of the aqueous samples.

RESULTS AND DISCUSSION

Packed Column GC-MS Analysis

13. Thiodiglycol, the major product identified in DRES mustard hydrolysate (5), was found at site #5 in the 1984, 1986 and 1987 aqueous samples. This hydrolysis product was the principal sample component and was present at 3.9 ± 0.2 mg/mL (n = 3), 0.60 ± 0.05 mg/mL (n = 3) and 2.2 ±0.3 mg/mL (n = 3) in samples 84–5, 86–5 and 87–5 respectively. Thiodiglycol levels in other samples, if present, were below the packed column GC-FID detection limit of 0.03 mg/mL (S/N = 3:1). 1-Oxa-4-thiane and 1,4-dithiane, noted during previous hydrolysate study (6), were also observed.

Capillary Column GC Analysis

14. Aqueous samples were extracted with hexane in order to concentrate mustard and other organic solubles prior to capillary column GC-FID and GC-MS analysis. Mustard, if present, was below the GC-FID detection limit of 0.2 μg/mL (S/N = 3:1) in all samples. However, a number of other compounds were identified in the aqueous samples from sites 5 and 6. Figures 1 to 5 illustrate total-ion-current chromatograms for samples 87 – 5, 87 – 6, 84 – 5, 84 – 5 and 86 – 5 respectively under electron impact (EI) or chemical ionization (CI) conditions.

15. Comparison of GC retention and EI mass spectral data with data acquired during the analysis of mustard hydrolysate (6) and munitions grade mustard samples (7, 8) were sufficient for the identification of several aqueous sample components including 1-oxa-4-thiane, 1,4-dithiane and 1,2,5-trithiapane. Most of the other extract components, listed in Table II, could not be identified in this manner and were identified (or tentatively identified) by interpretation of the EI and CI mass spectral data illustrated in Figures 6 to 25 inclusive. Isobutane CI mass spectral data provided molecular ion and CI fragmentation ion data for most of the sample components characterized during EI analysis. Additional mass spectral data were obtained for sufficiently basic compounds under ammonia CI conditions.

16. The MS data, while satisfactory for the characterization of many components, was insufficient for the identification of several vinyl alcohols and macrocyclic compounds. Complementary data, obtained by sample extract derivatization and analysis of extracts by capillary column GC-FTIR, resolved some of the ambiguities and enabled the identification of several novel vinyl alcohols in the presence of ether/thioether macrocycles with the same molecular formula. Discussion of the derivatization and FTIR spectra follows the mass spectral data.

a. Mass Spectral Data

17. Several of the lower molecular weight ring compounds were identified by comparison of the acquired mass spectral data with previously published results. The EI and isobutane CI mass spectra of 1-oxa-4-thiane (Figure 6) and 1,4-dithiane (Figure 10) were similar to data acquired during munitions grade mustard analysis (7, 8).

EI data for 1,3-dithiolane (Figure 8) correlated well with EPA/NIH data (11), while the EI mass spectrum of 1,2,5-trithiapane (Figure 15) was similar to previous reports (6, 12). Comparison of the EI and isobutane CI data obtained for 1,2,5-trithiapane with that acquired for sample peak number 6 (Figure 11) suggested the presence of an oxygen analogue of 1,2,5-trithiapane, 1-oxa-4,5-dithiapane. Both compounds exhibited intense $(M+H)^+$ pseudo-molecular ions during CI analysis and similar EI fragmentatin ions. A comparison with possible EI ion identities follows:

PRINCIPAL EI IONS	% RELATIVE INTENSITY	
	1-oxa-4,5-dithiapane	1,2,5-trithiapane
$M^{+\cdot}$	100	100
$(M-C_2H_4)^{+\cdot}$	10	22
$(C_2H_4S_2)^{+\cdot}$	27	20
$(M-CH_2S)^+$	15	20
$(M-CH_3S)^+$	30	10
$(CH_2S_2)^{+\cdot}$	30	20
$(C_2H_4S)^{+\cdot}$	97	45
$(CHS)^+$	47	25

18. Seven macrocyclic compounds containing ether and thioether linkages were tentatively identified by interpretation of the FTIR spectra and the mass spectral data contained in Figures 12, 16, 19, 21, 22, 23, 24 and 25. All the macrocyclic compounds exhibited molecular ions and characteristic fragmentation ions under EI conditions. Molecular weight assignment was confirmed for most macrocycles by the presence of pseudo-molecular ions during ammonia and/or isobutane CI-MS analysis.

19. Macrocyclic compounds have attracted considerable scientific interest due to their ability to act as ligands for the complexation of metal cations (13). Synthetic procedures for a number of different macrocycles have been reviewed (14 – 16). The EI mass spectra (17 – 24) of macrocyclic compounds often exhibit molecular ions and are characterized by fragmentation ions due to loss of C_2H_4X (where X = O or S) units. CI mass spectral reports (25 – 28) appear to be limited to crown ether compounds.

20. Many of the ether/thioether macrocyclic compounds identified in the hexane extracts have been previously synthesized by several groups (29 – 33). Meadow and Reid (29) reported the synthesis of 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane while Dann *et al.* (30) has synthesized 1,7-dioxa-4,10-dithiacyclodecane. Synthetic procedures for most of the remaining macrocycles have been reported by Bradshaw *et al.* (31, 32). The EI mass spectra of these compounds does not appear to have been published.

21. The mass spectra of 1,4-dioxa-7-thionane, 1-oxa-4,7-dithionane, 1,4-dioxa-7,10-dithiacyclododecane, 1,7-dioxa-4,10-dithiacyclododecane, 1-oxa-4,7,10-trithiacyclododecane, 1,7-dioxa-4,10,13-trithiacyclopentadecane, 1-oxa-4,7,10,13-tetrathiacyclopentadecane and 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane identified in the aqueous extracts are illustrated in Figures 12, 16, 19, 21, 22, 23, 24 and 25 respectively. The EI mass spectra, like their crown ether analogues, exhibited molecular ions and fragmentation ions due to loss of C_2H_4X or C_2H_3X (where X = O or S) units. A low mass ion due to $(C_2H_5X)^+$, $(C_4H_6S)^{+\cdot}$ or $(C_4H_7S)^+$ was usually the base ion in these EI mass spectra. The following summary illustrates the principal higher mass EI ions and their relative intensities for the macrocycles referred to as peak numbers 7, 12, 15, 17, 18, 19, 20 and 23 in Table II.

PRINCIPAL EI IONS	% RELATIVE INTENSITY (> 5%)							
Peak No.	7	12	15	17	18	19	20	23
No. of S Atoms	1	2	2	2	3	3	4	4
No. of O Atoms	2	1	2	2	1	2	1	2
$M^{+\cdot}$	25	48	30	18	28	13	34	10
$(M-C_2H_3O)^+$	100	22	–	–	–	–	–	–
$(M-C_2H_4O)^{+\cdot}$	–	–	5	5	–	–	–	–
$(M-C_2H_3S)^+$	–	29	20	–	–	–	–	–
$(M-C_2H_4S)^{+\cdot}$	–	–	23	–	7	7	12	–
$(M-C_2H_4S-C_2H_2)^{+\cdot}$	–	–	–	–	10	15	26	6
$(M-(C_2H_4O)_2)^{+\cdot}$	–	–	18	–	–	–	–	–
$(M-C_2H_4S-C_2H_4O)^{+\cdot}$	–	–	–	–	22	20	18	18
$(M-(C_2H_4S)_2)^{+\cdot}$	–	–	–	–	–	–	25	9
$(M-(C_2H_4S)_2-H_2O)^{+\cdot}$	–	–	–	–	–	–	10	9
$(M-(C_2H_4S)_2-C_2H_4O)^{+\cdot}$	–	–	–	–	–	–	35	18
$(C_4H_9SO)^+$	100	29	33	55	34	85	42	54

22. Molecular weight of most ether/thioether macrocycles was confirmed during ammonia and isobutane CI-MS. The CI mass spectra for these compounds, obtained primarily with ammonia, were dominated by $(M+H)^+$ and/or $(M+NH_4)^+$ pseudo-molecular ions. Fragmentation ions were minor and largely due to neutral loss of C_2H_4X units from the pseudo-molecular ion.

23. Three vinyl alcohols related in structure to mustard, sesquimustard (Q) and bis[(2-chloroethyl)ethyl] ether (T) were identified after interpretation of mass spectral, infrared and derivatization data. The lowest molecular weight vinyl alcohol, related in structure to mustard, was first tentatively identified in mustard hydrolysate (6). Synthesis of this compound and comparison of the GC and MS data (Figure 7) with that obtained during aqueous sample analysis confirmed the presence of this compound.

24. The mass spectra of the two higher molecular weight vinyl alcohols related to Q and T are illustrated in Figures 17 and 20 respectively. Molecular ion intensity was significantly lower for the longer chain vinyl alcohol, (2-hydroxyethylthio)ethyl (vinylthio)ethyl ether. Both EI mass spectra were dominated by fragmentation ions at m/z 45, 61, 86, 87 and 105 due to $(C_2H_5O)^+$ or $(CH_3S)^+$, $(C_2H_5S)^+$, $(C_4H_6S)^{+\cdot}$, $(C_4H_7S)^+$ and $(C_4H_9SO)^+$ respectively. The molecular weight of (2-hydroxyethylthio)ethyl vinyl sulfide, the vinyl alcohol related to Q was confirmed by the presence of $(M+H)^+$ pseudo-molecular ions under both isobutane and ammonia CI conditions. (2-Hydroxy-thylthio)ethyl (vinylthio)ethyl ether exhibited pseudo-molecular ions under ammonia CI conditions but with considerably more CI fragmentation than (2-hydroxyethylthio)ethyl vinyl sulfide.

25. Bis(2-chloroethyl) ether (Figure 9) and the complete dehydrochlorination product of T, bis(vinylthio)ethyl ether (Figure 18), were identified by comparison of EI and/or isobutane CI data with previous published reports (7, 8, 11). Ammonia CI data for bis(2-chloroethyl) ether was similar to that obtained for mustard (34). This compound, sufficiently basic to form only an $(M+NH_4)^+$ adduct ion during ammonia CI-MS, did exhibit a base ion due to $(M+H)^+$ under isobutane CI conditions. Bis(vinylthio)ethyl ether produced $(M+H)^+$, $(M+H\text{-}C_2H_4S)^+$ and $(M+H\text{-}C_2H_4S\text{-}C_2H_4O)^+$ CI ions with both reagent gases. Several other compounds in the aqueous extracts remain unknown.

b. TMS Sample Extract Derivatization

26. Further evidence for the presence of vinyl alcohols in the aqueous extracts was provided by trimethylsilyl (TMS) derivatization. Figure 26 illustrates the chromatogram obtained after derivatization of sample 87 – 5 with bis(trimethylsilyl)trifluoroacetamide (BSTFA) catalyzed with 1% trimethylchlorosilane according to the method of Butts (35). Chromatographic peaks due to the vinyl alcohols were not observed, but in their place

three TMS derivatized vinyl alcohols were observed. Figures 27, 28 and 29 illustrate the EI and ammonia CI mass spectra obtained for the TMS derivatives of (2-vinylthio)-ethanol, (2-hydroxyethylthio)ethyl vinyl sulfide and (2-hydroxyethylthio)ethyl (vinylthio)ethyl ether respectively. Trace molecular ions, observed during EI study, were confirmed by the presence of $(M+H)^+$ and/or $(M+NH_4)$ pseudo-molecular ions. EI fragmentation ions at m/z 73, 87, 116, 117 and 177 were likely due to $((CH_3)_3Si)^+$, $(C_4H_7S)^+$, $(C_2H_3OTMS)^{+\cdot}$, $(C_2H_4OTMS)^+$ and trimethylsilylated 1-oxa-4-thiane respectively.

27. The other sample components identified in Table II did not form derivatives, a fact consistent with the presence of compounds without active hydrogen sites. This evidence suggested that the other compounds with the same elemental formulae as the vinyl alcohols were macrocyclic.

c. Infrared Data

28. Capillary column GC-FTIR analysis of 84 – 5 (Figure 30) provided additional structural evidence for several of the identified compounds. The requirement for larger amounts of analyte (ca 100 ng) limited application of capillary column GC-FTIR to the more abundant extract components (Figure 31). Bis(2-chloroethyl)ether (Figure 31b) and 1,4-dithiane (Figure 31c) exhibited IR spectra similar to that stored in the EPA vapour phase library (36). Spectral similarities were noted for 1,4-dithiane and 1,2,5-trithiapane (Figure 31c and f). The most recognizable features were the two bands at 1270 – 1280 cm^{-1} and 1410 – 1420 cm^{-1} due to the thioether linkage, and the characteristic shape of the cyclic aliphatic hydrocarbon bands at 2800 – 3000 cm^{-1}. The spectra of 1-oxa-4-thiane and 1-oxa-4,5-dithiapane (Figure 31a and d) were also similar although they contained the additional strong cyclic ether band at 1110 – 1120 cm^{-1}.

29. The IR spectra of the macrocycles illustrated in Figures 31g, i and j were similar to that obtained for 15-crown-5, a crown ether tabulated in the Aldrich neat library (37). Cyclic ether linkages were evidenced by a band centered around 1110 cm^{-1} as opposed to 1120 cm^{-1} for open chain ethers, while cyclic aliphatic structure was supported by the general band shape in the 2800 – 3000 cm^{-1} region. Thioether linkages were evidenced by less intense bands at 1270 – 1280 cm^{-1} and 1410 – 1420 cm^{-1}. Also, the lack of any alkene stretch bands between 1580 – 1600 cm^{-1}, and the lack of hydroxyl bands at

3400 – 3600 cm^{-1} and 1020 – 1050 cm^{-1} precluded the presence of open chain vinyl alcohols. The IR spectra of the vinyl alcohol, (2-hydroxyethylthio)ethyl(vinylthio)ethyl ether (Figure 31h), although similar to the macrocycles due to the presence of aliphatic and ether/thioether linkages, contained bands at 1588 cm^{-1} and 1044 cm^{-1} due to the alkene and hydroxyl structure. Aliphatic structure between 2800 – 3000 cm^{-1} region was also typical of straight chain hydrocarbons.

30. (2-Vinylthio)ethanol exhibited a strong band at 1054 cm^{-1} due to the hydroxyl group and has a typical band shape for straight chain aliphatic structure in the 2900 cm^{-1} region. Figure 32 illustrates the FTIR spectrum obtained for synthetic (2-vinylthio)ethanol.

CONCLUSIONS

31. Thiodiglycol and twenty-four mustard related compounds were identified in aqueous samples containing mustard hydrolysate by capillary column GC-MS and GC-FTIR. Many of these compounds, most notably the vinyl alcohols and ether/thioether macrocycles, have not been previously characterized or have not been associated with mustard decomposition. Mustard was not detected in any of the aqueous samples.

32. The electron impact and chemical ionization mass spectral data acquired may prove valuable for the analysis of samples suspected to contain mustard, its impurities or decomposition products. These data could be particularly useful for the identification of these compounds in weathered samples where the original sulfur vesicant(s) have undergone extensive decomposition.

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TABLE I

a) GC-MS OPERATING CONDITIONS

GC-MS INTERFACE:	Jet Separator (230°C): Packed Column GC-MS Direct (230°C): Capillary Column GC-MS		
IONIZATION MODE:	Electron Impact	Isobutane CI[1]	Ammonia CI[2]
ELECTRON ENERGY:	70 eV	150 eV	50 eV
EMISSION:	100 μA	500 μA	500 μA
SOURCE TEMPERATURE:	200°C	110 – 140°C[3]	140 – 150°C[3]
SOURCE PRESSURE:	2×10^{-6} torr	2×10^{-4} torr	5×10^{-5} torr
SCAN FUNCTION and RATE:	500 to 40 u, exponential down, 1 sec/decade		
ACCELERATING VOLTAGE:	6 kV	6 kV	6 kV
RESOLUTION (10% Valley Definition):	1000	1000	1000

[1] 99% (Pure Grade) Isobutane (Liquid Carbonics Canada Ltd., Scarborough, Ontario)

[2] 99.99% (Anhydrous Grade) Ammonia (Liquid Carbonics Ltd.)

[3] Source temperature increased over the analysis period due to heating of the block by the filament.

b) GC-FTIR OPERATING CONDITIONS

GC-IR INTERFACE:	Heated gold coated light pipe (300°C) 1.0 mm ID × 16 cm dimensions
GC-CONDITIONS:	J & W 60 meter DB-5 wide bore capillary column 50°C (2 min), 10°C/min, 280°C (10 min) in splitless mode. Flow rate = 2.5 mL/min with 1.5 mL/min make-up gas added at light pipe.
NUMBER OF SCANS/FILE:	8 scans for 2.12 sec measurement time
RESOLUTION:	2048 transform points for 8 cm^{-1} resolution
DETECTOR:	short range Mercury Cadmium Telluride (MCT)

Table II

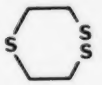
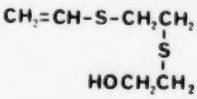
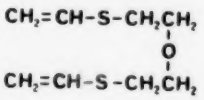
COMPOUNDS IDENTIFIED IN GROUND WATER SAMPLE EXTRACTS

Chromatogram Peak Number[1]	Mol Wt	Compound	Sample Presence				MS Data
			84-5	86-5	87-5	87-6	
1	104	1-Oxa-4-thiane	✓	✓	✓	✓	Fig. 6
2	104	(2-Vinylthiol)ethanol $CH_2=CH-S-CH_2CH_2OH$	✓	—	✓	—	Fig. 7
3	106	1,3-Dithiolane	✓	✓	✓	✓	Fig. 8
4	142	Bis(2-chloroethyl)ether $(ClCH_2CH_2)_2O$	✓	✓	✓	—	Fig. 9
5	120	1,4-Dithiane	✓	✓	✓	✓	Fig. 10
6	136	1-Oxa-4,5-dithiapane[2]	✓	✓	✓	✓	Fig. 11
7	148	1,4-Dioxa-7-thionane[2]	✓	✓	✓	—	Fig. 12
8	166	(2-Chloroethylthio)ethyl vinyl ether[2] $ClCH_2CH_2-S-CH_2CH_2-O-CH=CH_2$	✓	✓	✓	—	Fig. 13

.../2

Table II (Cont'd)

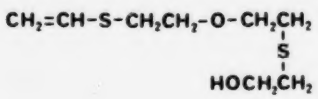
COMPOUNDS IDENTIFIED IN GROUND WATER SAMPLE EXTRACTS

Chromatogram Peak Number[1]	Mol Wt	Compound	Sample Presence				MS Data
			84-5	86-5	87-5	87-6	
9	162	Unknown	✓	—	✓	—	Fig. 14
10	164	Unknown	✓	✓	✓	—	Fig. 14
11	152	1,2,5-Trithiapane 	✓	✓	✓	✓	Fig. 15
12	164	1-Oxa-4,7-dithionane[2]	✓	✓	✓	—	Fig. 16
13	164	(2-Hydroxyethylthio)ethyl vinyl sulfide[2] 	✓	—	✓	—	Fig. 17
14	190	Bis(vinylthio)ethyl ether[2] 	✓	✓	✓	—	Fig. 18
15	208	1,4-Dioxa-7,10-dithiacyclododecane[2]	✓	—	✓	—	Fig. 19

.../3

Table II (Cont'd)

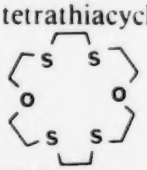
COMPOUNDS IDENTIFIED IN GROUND WATER SAMPLE EXTRACTS

Chromatogram Peak Number[1]	Mol Wt	Compound	Sample Presence				MS Data
			84-5	86-5	87-5	87-6	
16	208	(2-Hydroxyethylthio)ethyl (vinylthio)ethyl ether[2] 	✓	—	✓	—	Fig. 20
17	208	1,7-Dioxa-4,10-dithiacyclo-dodecane[2]	✓	✓	✓	✓	Fig. 21
18	224	1-Oxa-4,7,10-trithia-cyclododecane[2]	✓	✓	✓	✓	Fig. 22
19	268	1,7-Dioxa-4,10,13-trithia-cyclopentadecane[2]	✓	✓	✓	✓	Fig. 23
20	284	1-Oxa-4,7,10,13-tetrathia-cyclopentadecane[2]	—	—	✓	—	Fig. 24
21		Unknown	—	—	✓	—	Fig. 24

.../4

Table II (Cont'd)

COMPOUNDS IDENTIFIED IN GROUND WATER SAMPLE EXTRACTS

Chromatogram Peak Number[1]	Mol Wt	Compound	Sample Presence				MS Data
			84-5	86-5	87-5	87-6	
22	390	Dioctyl phthalate	Solvent Impurity				
23	328	1,10-Dioxa-4,7,13,16-tetrathiacyclooctadecane[2] 	—	—	✓	—	Fig. 25
24		Unknown	—	—	✓	—	Fig. 25
25		TMS derivative of (2-vinylthio)ethanol TMS-O-CH_2CH_2-S-CH=CH_2	TMS derivatized 87 – 5				Fig. 27
26		TMS derviative of (2-hydroxy-ethylthio)ethyl vinyl sulfide[2] TMS-O-CH_2CH_2-S-CH_2CH_2-S-CH=CH_2	TMS derivatized 87 – 5				Fig. 28
27		TMS derivative of (2-hydroxy-ethylthio)ethyl (vinylthio)ethyl ether[2] TMS-O-CH_2CH_2-S-CH_2CH_2 O CH$_2$=CH-S-CH_2CH_2	TMS derivatized 87 – 5				Fig. 29

[1] Refer to Figures 1, 2, 3, 4, 5, 26 and 30

[2] Tentative identification based on interpretation of EI and CI mass spectral data and GC retention behaviour

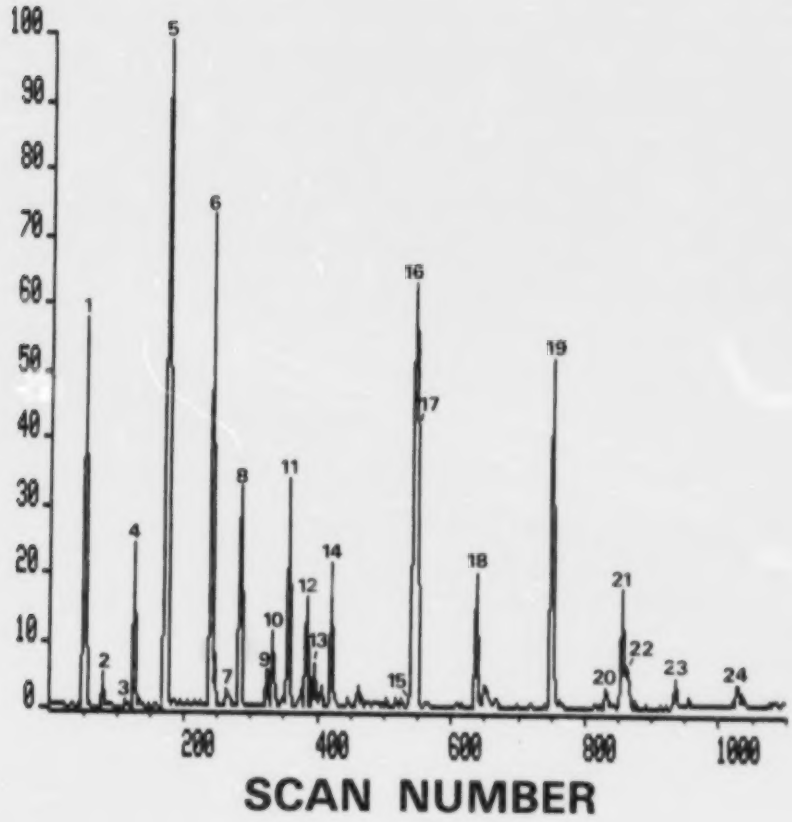


Figure 1

Capillary Column GC-MS (EI) Total-Ion-Current (350 to 40 u) Chromatogram of Hexane Extract of Ground Water Sample 87-5. (15 m × 0.32 mm ID J+W DB-5; 40° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.5 sec). Numbered Peaks are Identified in Table II.

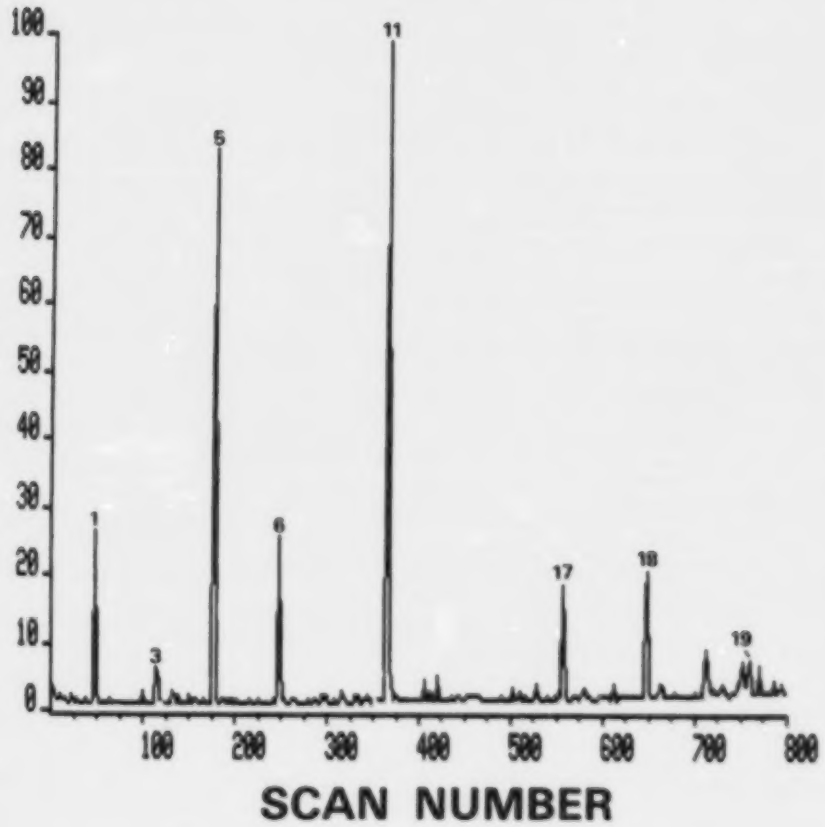


Figure 2

Capillary Column GC-MS (EI) Total-Ion-Current (400 to 60 u) Chromatogram of Hexane Extract of Ground Water Sample 87-6. (15 m × 0.32 mm ID DB-5; 40° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.6 sec). Numbered Peaks are Identified in Table II.

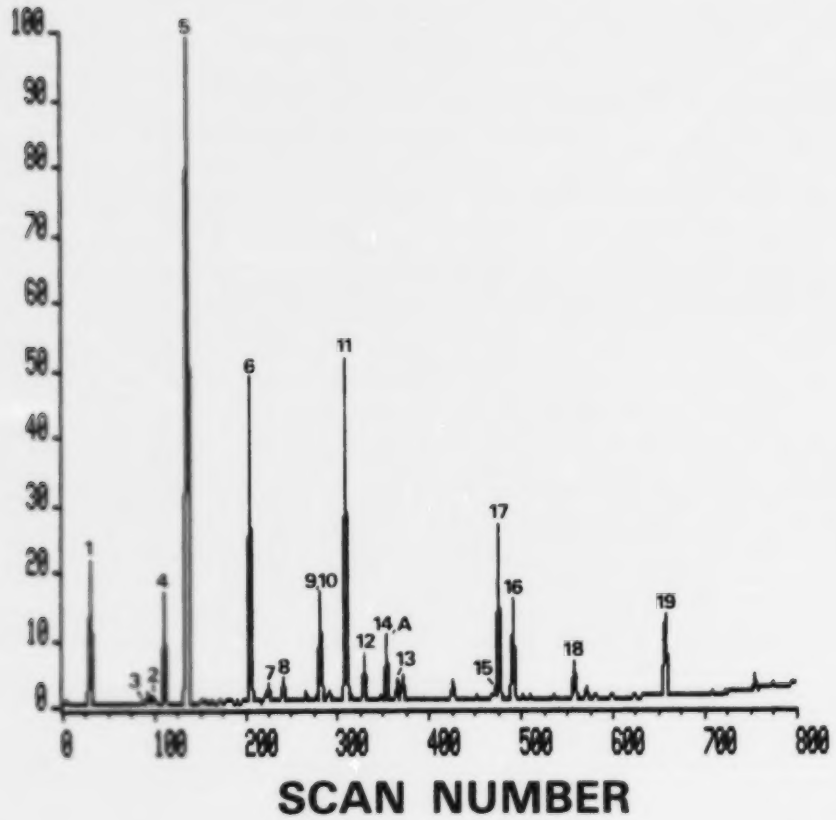


Figure 3

Capillary Column GC-MS (EI) Total-Ion-Current (600 to 100 u) Chromatogram of Hexane Extract of Ground Water Sample 84-5. (15 m × 0.32 mm ID J+W DB-1701; 50° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.6 sec). Numbered Peaks are Identified in Table II.

(A = nC_{16} – alkane added to sample)

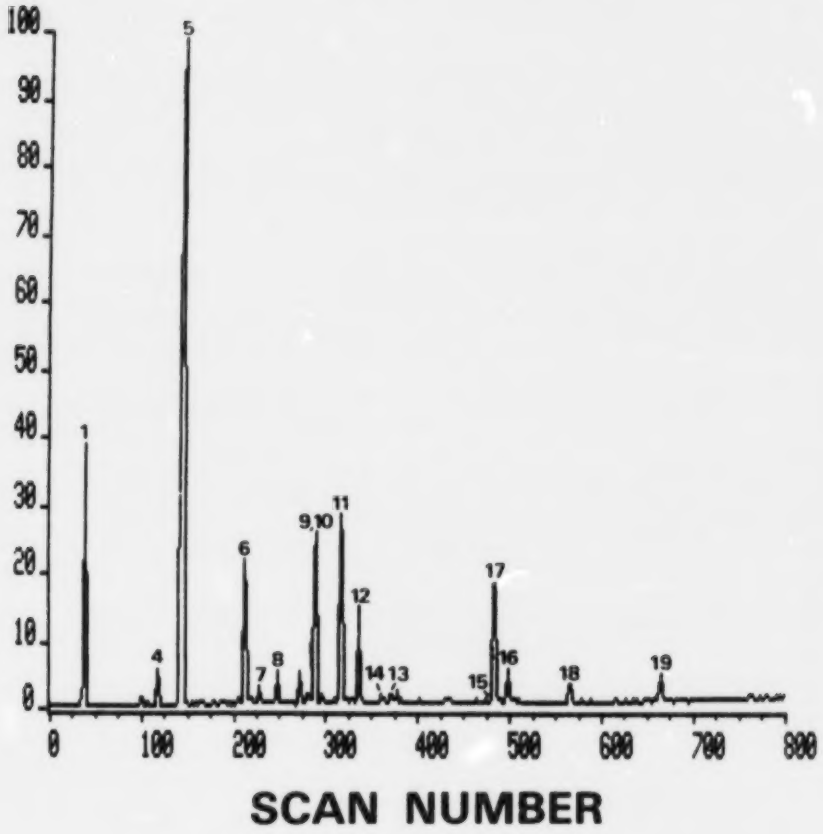


Figure 4

Capillary Column GC-MS (Ammonia CI) Total-Ion-Current (600 to 100 u) Chromatogram of Hexane Extract of Ground Water Sample 84-5. (15 m × 0.32 mm ID J+W DB-1701; 50° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.6 sec). Numbered Peaks are Identified in Table II.

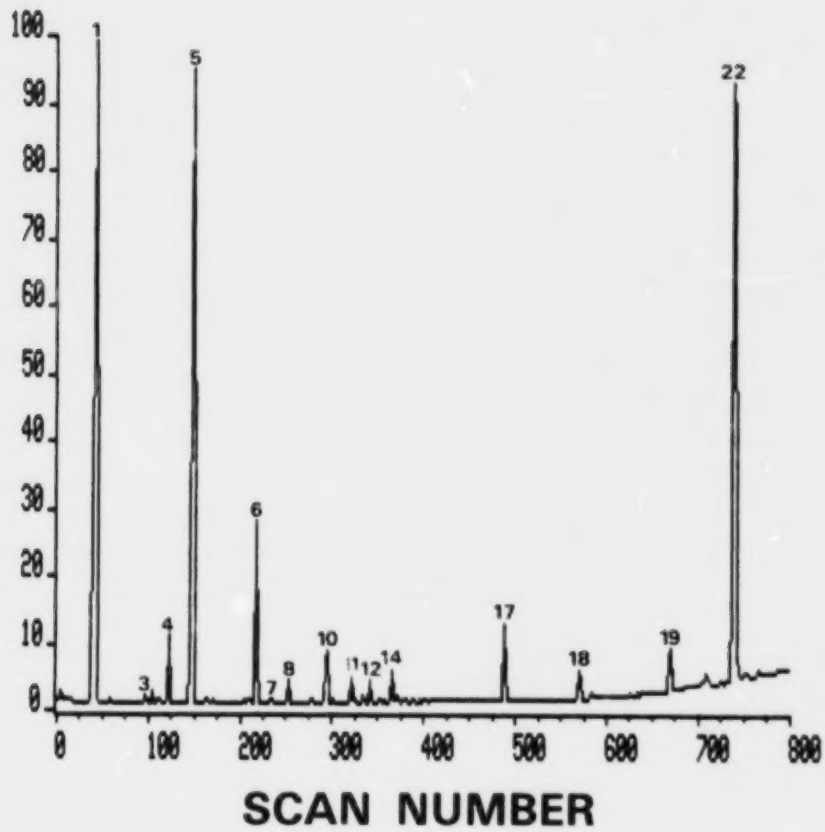


Figure 5

Capillary Column GC-MS (EI) Total-Ion-Current (600 to 40 u) Chromatogram of Hexane Extract of Ground Water Sample 86-5. (15 m × 0.32 mm ID J+W DB-1701; 50° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.6 sec). Numbered Peaks are Identified in Table II.

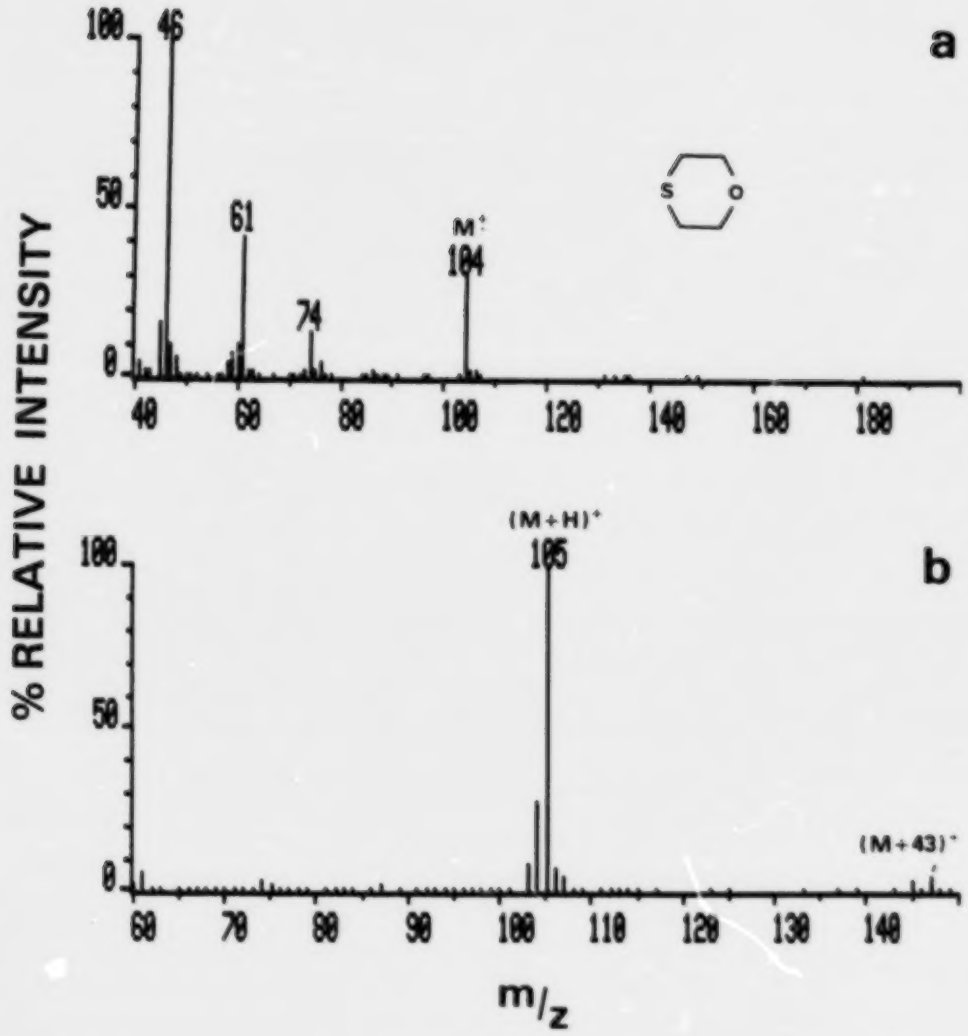


Figure 6

a) EI; and b) Isobutane CI Mass Spectra of 1-Oxa-4-thiane (Peak Number 1)

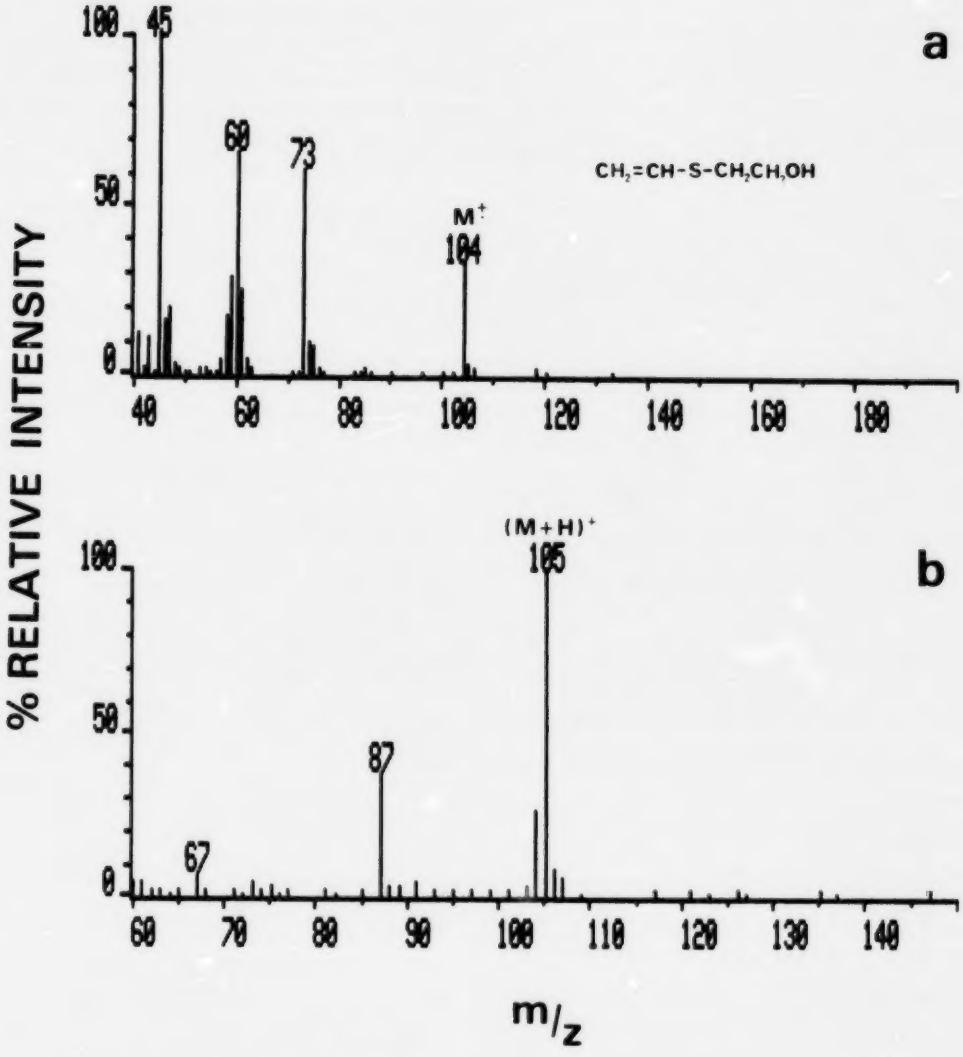


Figure 7

a) EI; and b) Isobutane CI Mass Spectra of (2-Vinylthio)ethanol (Peak Number 2)

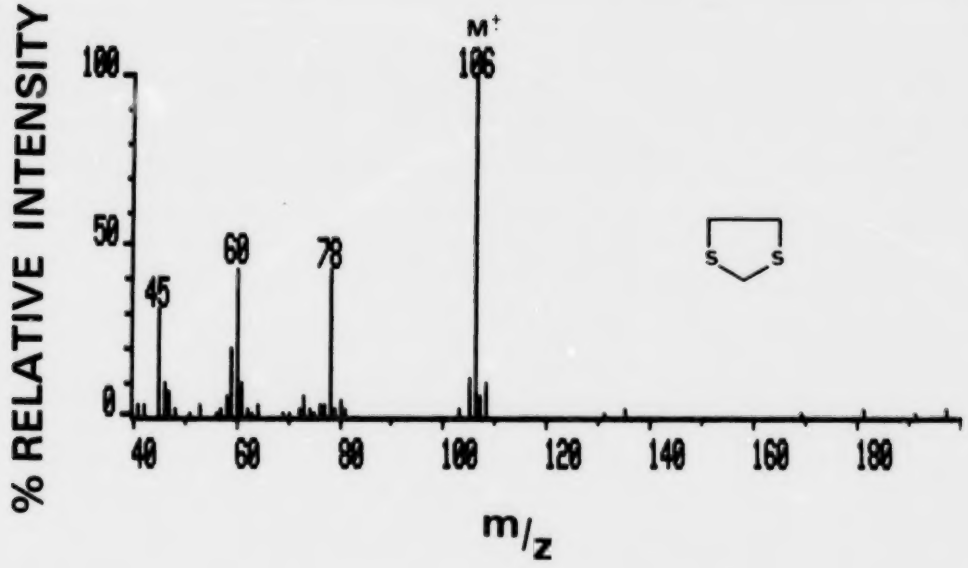


Figure 8

EI Mass Spectra of 1,3-Dithiolane (Peak Number 3)

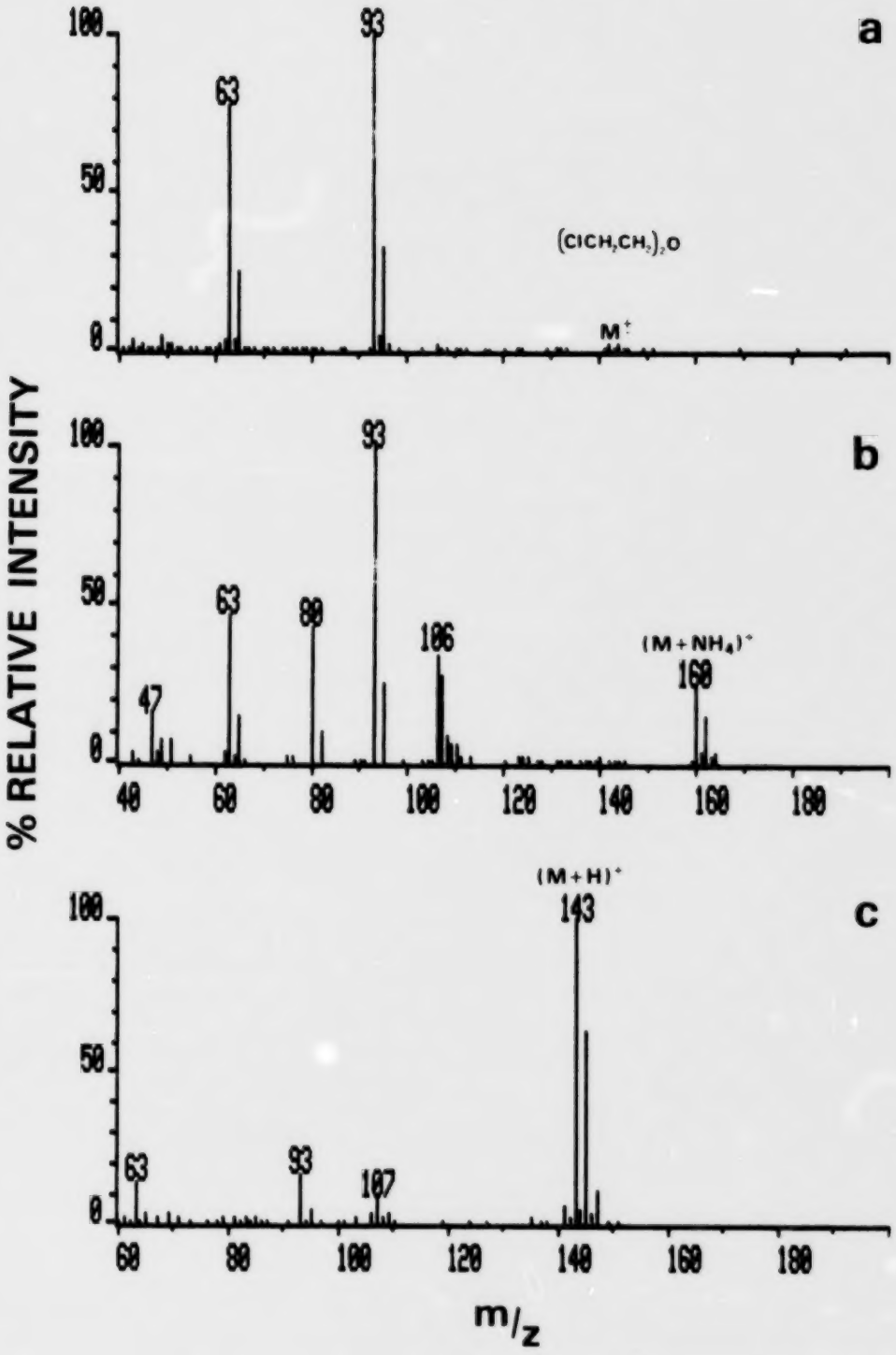


Figure 9

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of Bis(2-chloroethyl) ether (Peak Number 4)

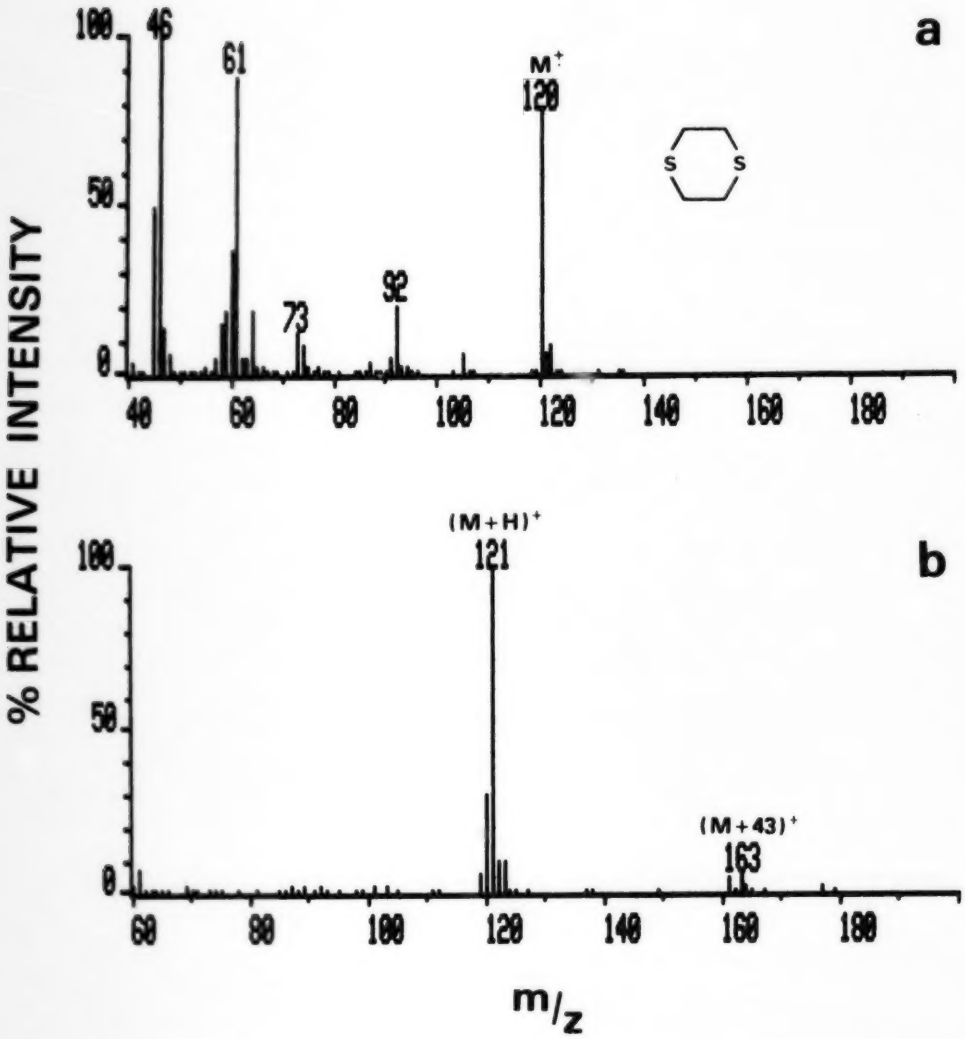


Figure 10

a) EI; and b) Isobutane CI Mass Spectra of 1,4-Dithiane (Peak Number 5)

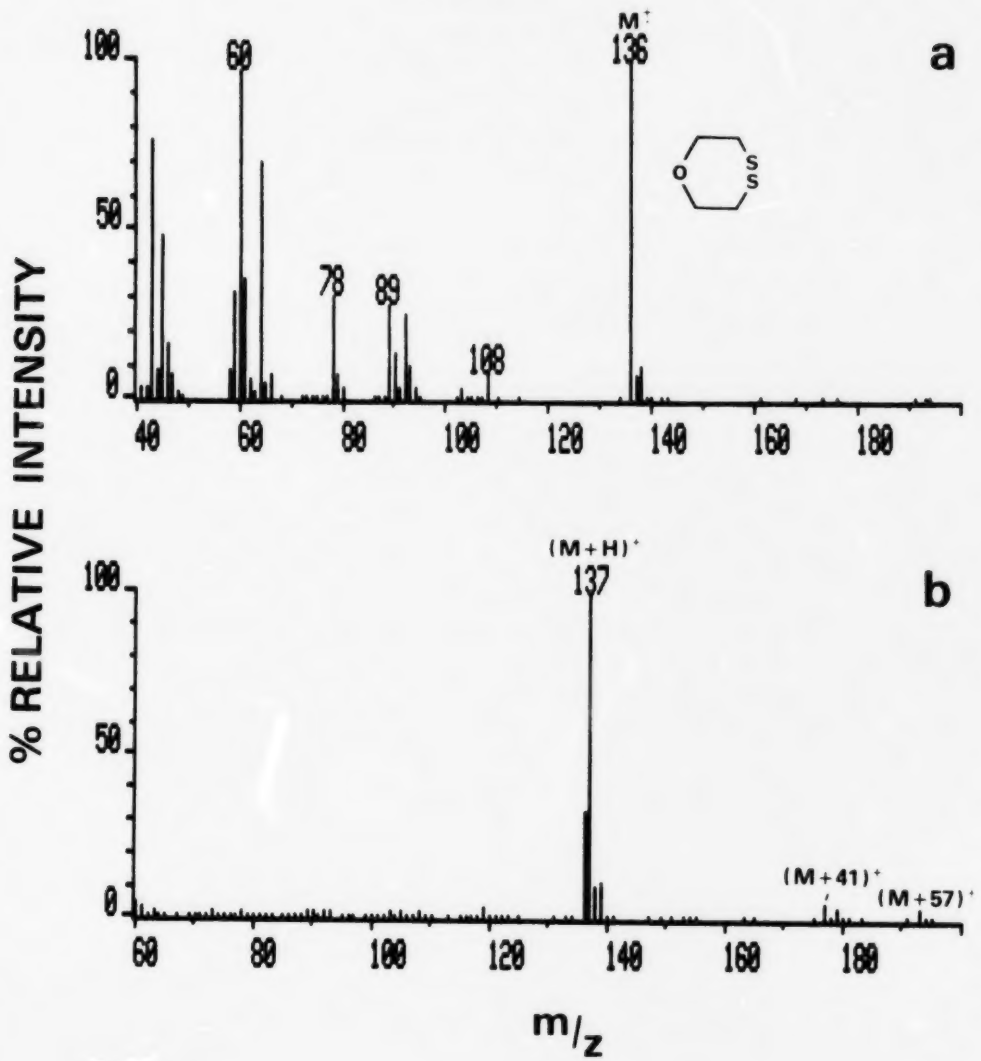


Figure 11

a) EI; and b) Isobutane CI Mass Spectra of 1-Oxa-4,5-dithiapane (Peak Number 6)

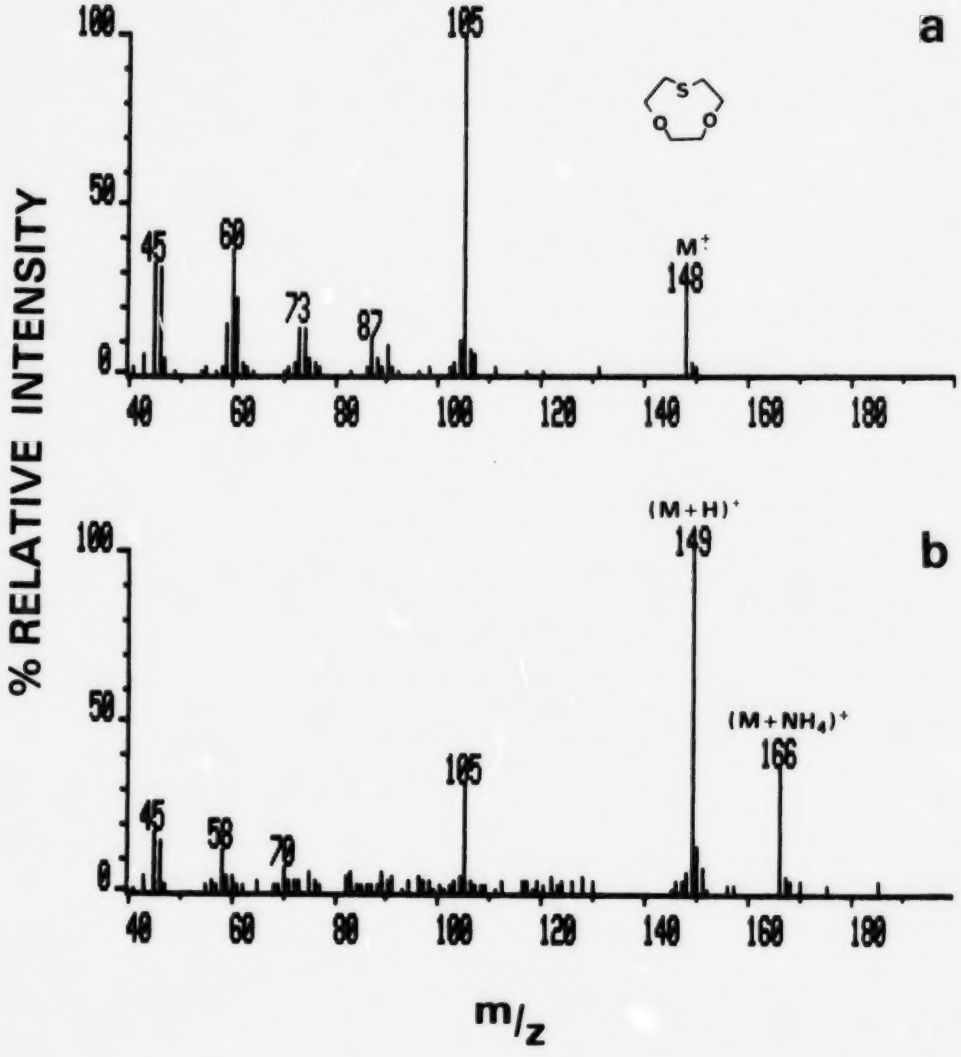


Figure 12

a) EI; and b) Ammonia CI Mass Spectra of 1,4-Dioxa-7-thionane (Peak Number 7)

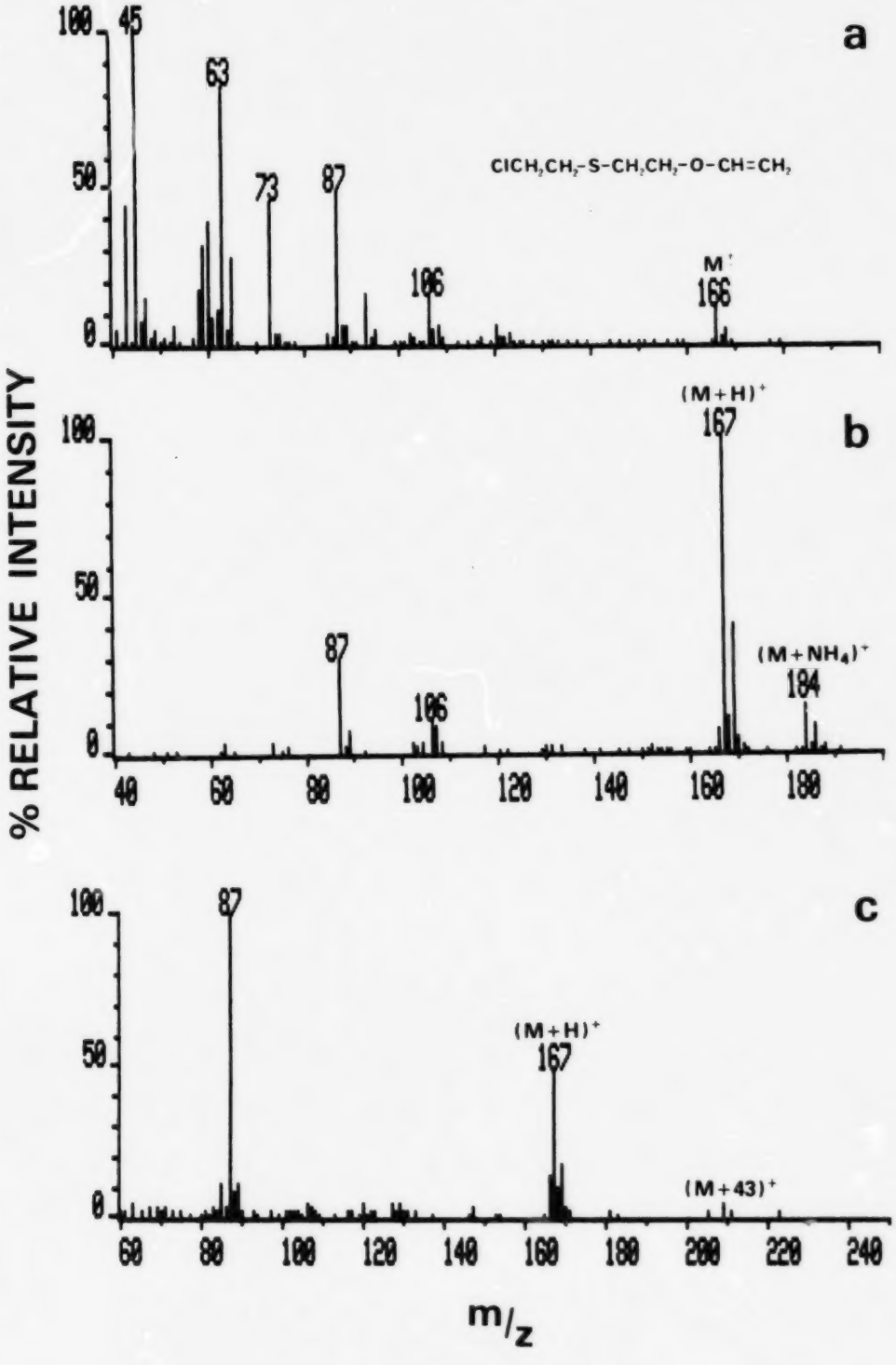


Figure 13

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of (2-Chloroethylthio)ethyl vinyl ether (Peak Number 8)

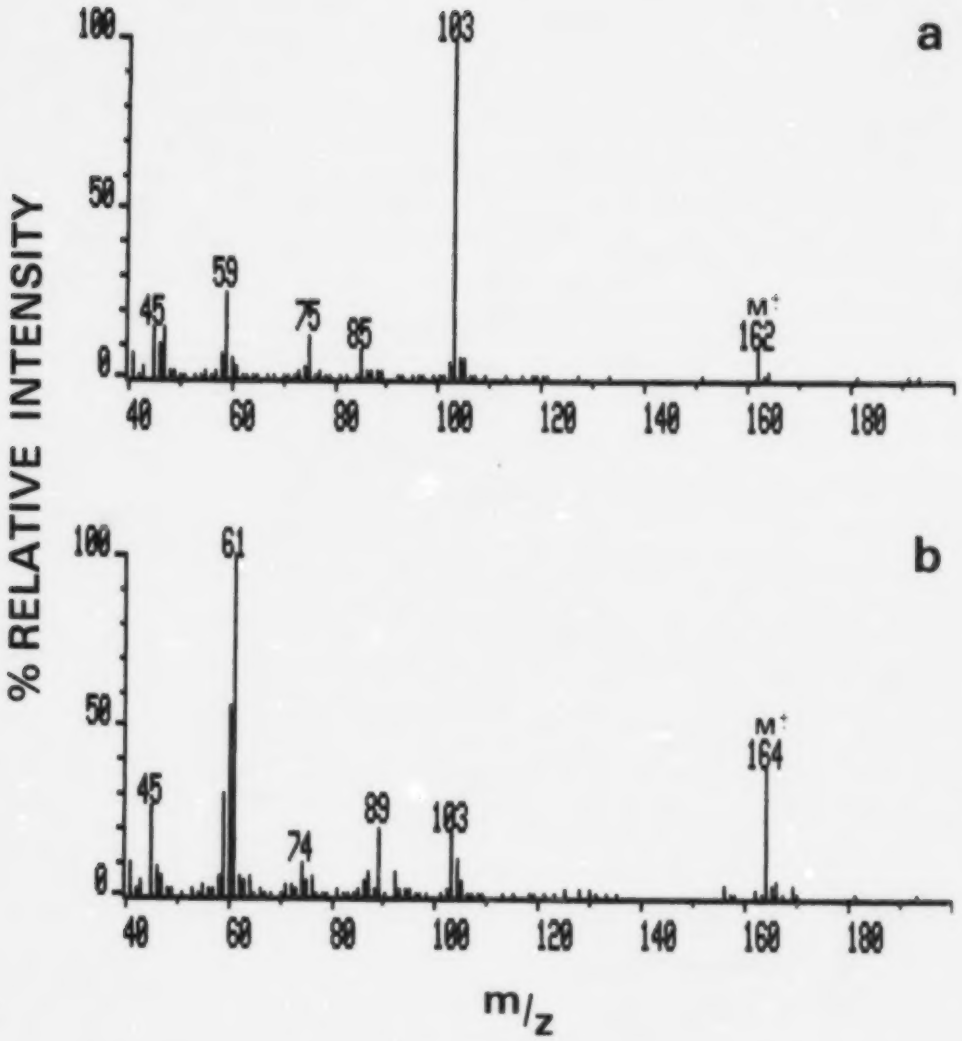


Figure 14

EI Mass Spectra of Unknowns with Molecular Weights of a) 162; and b) 164 (Peak Numbers 9 and 10)

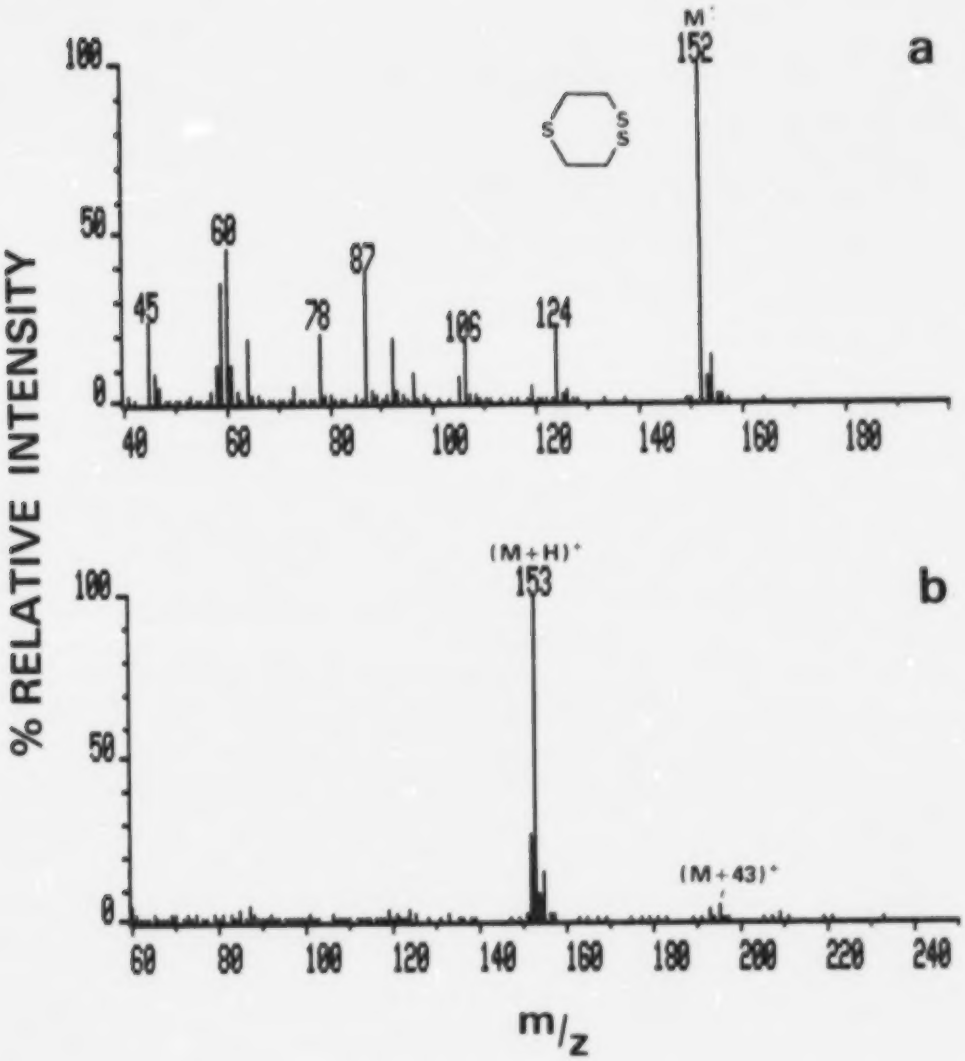


Figure 15

a) EI; and b) Isobutane CI Mass Spectra of 1,2,5-Trithiapane (Peak Number 11)

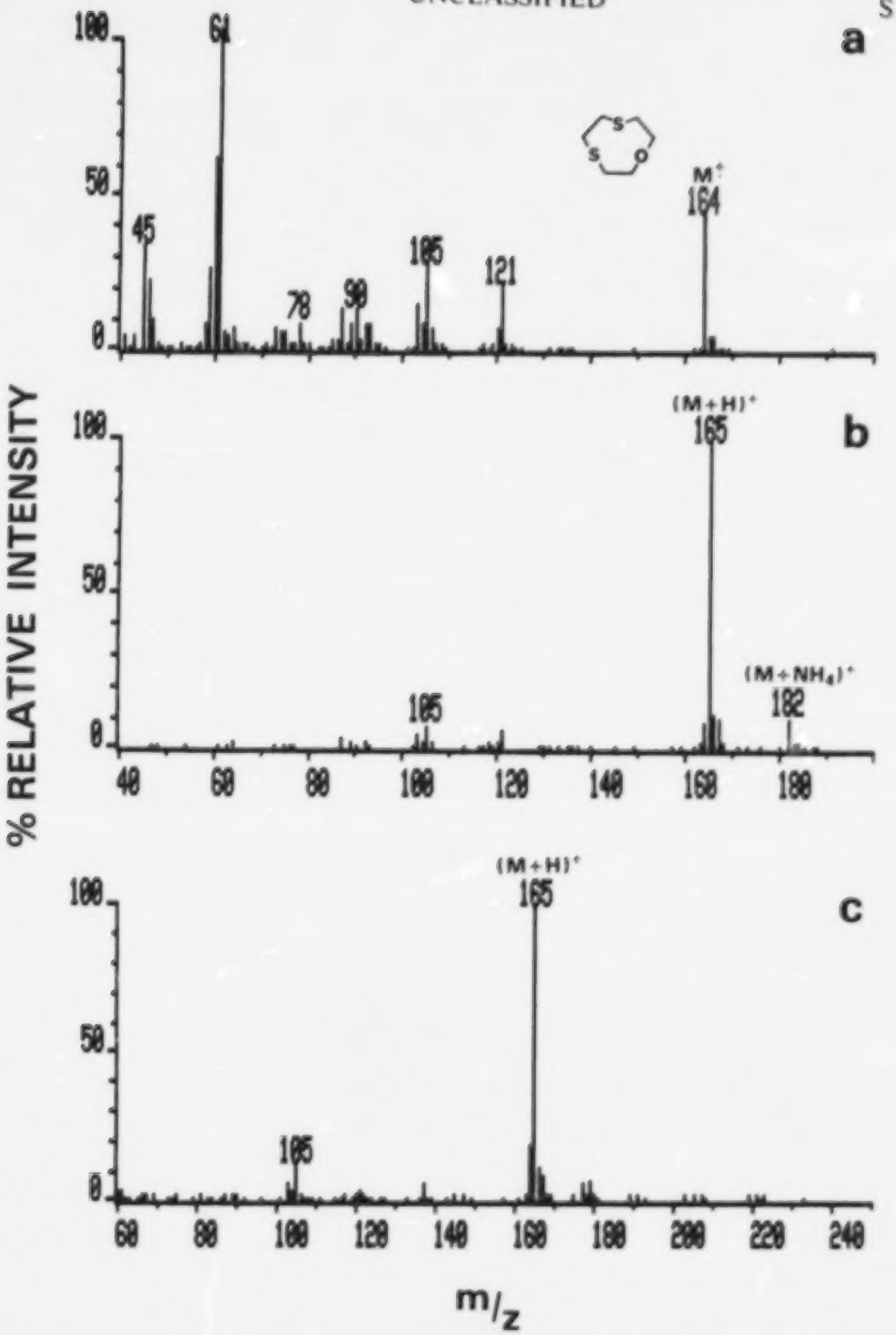


Figure 16

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of 1-Oxa-4,7-dithionane (Peak Number 12)

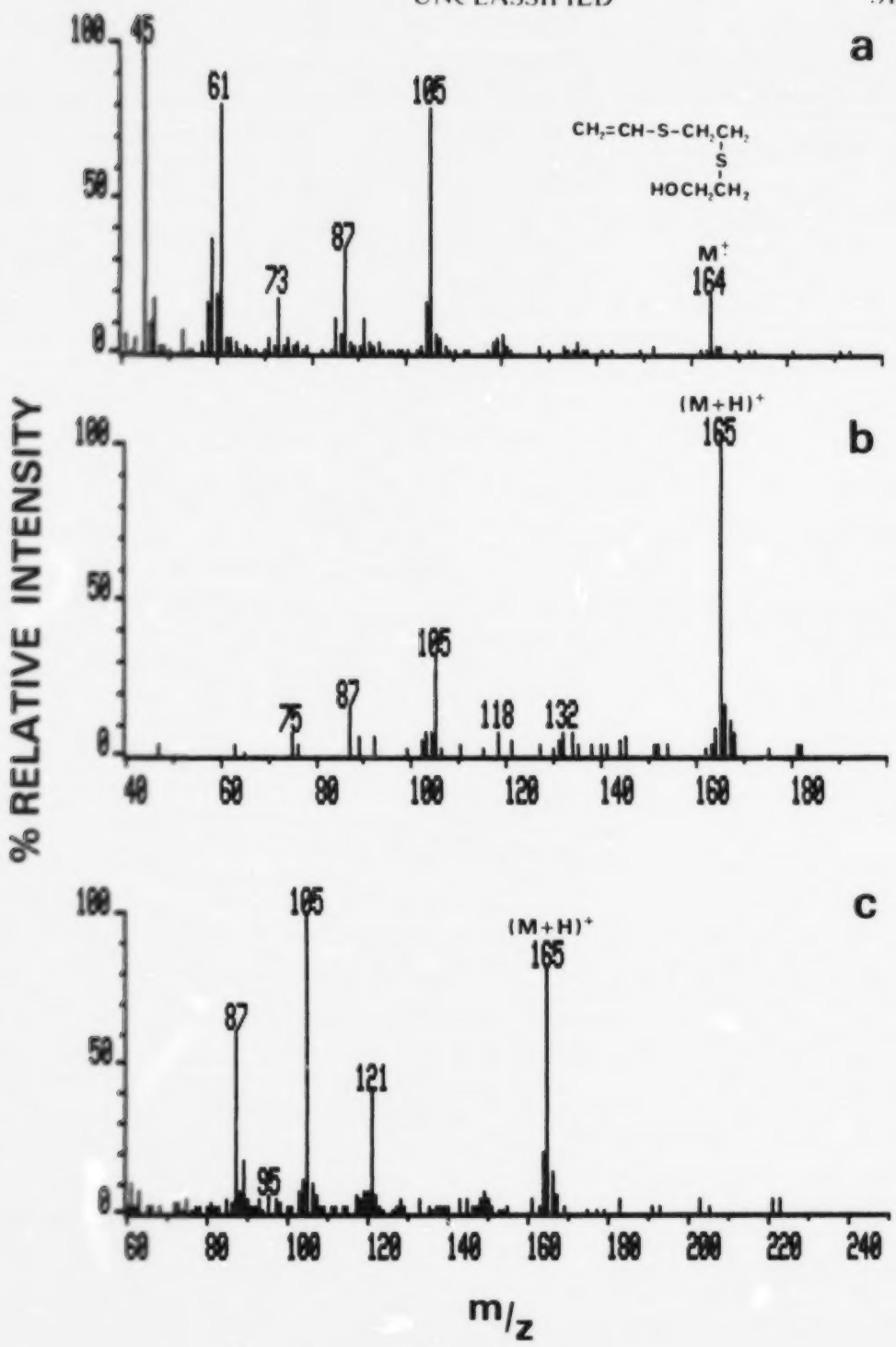


Figure 17

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of (2-Hydroxyethylthio)ethyl vinyl sulfide (Peak Number 13)

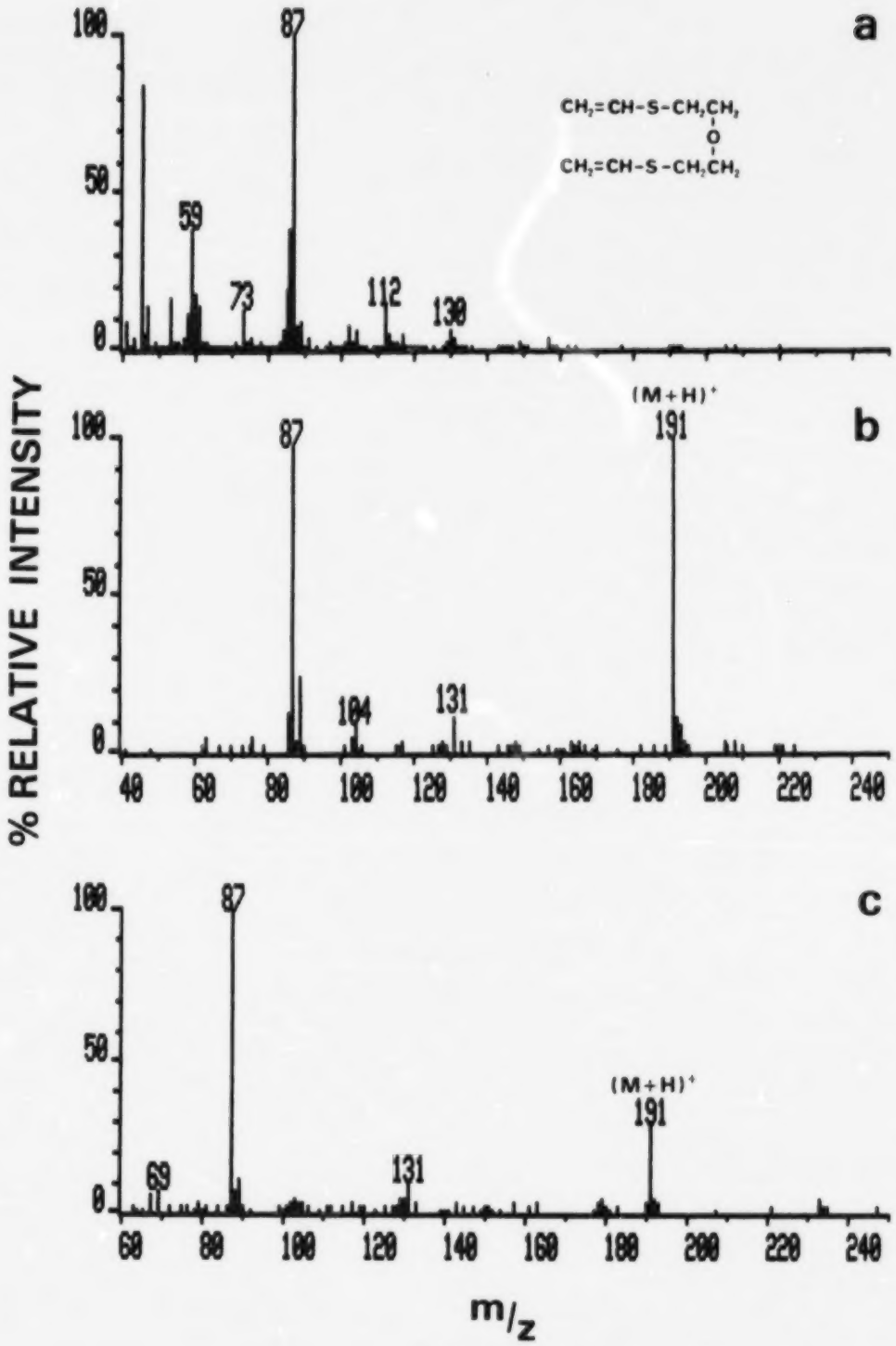


Figure 18

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of Bis(vinylthio)ethyl ether (Peak Number 14)

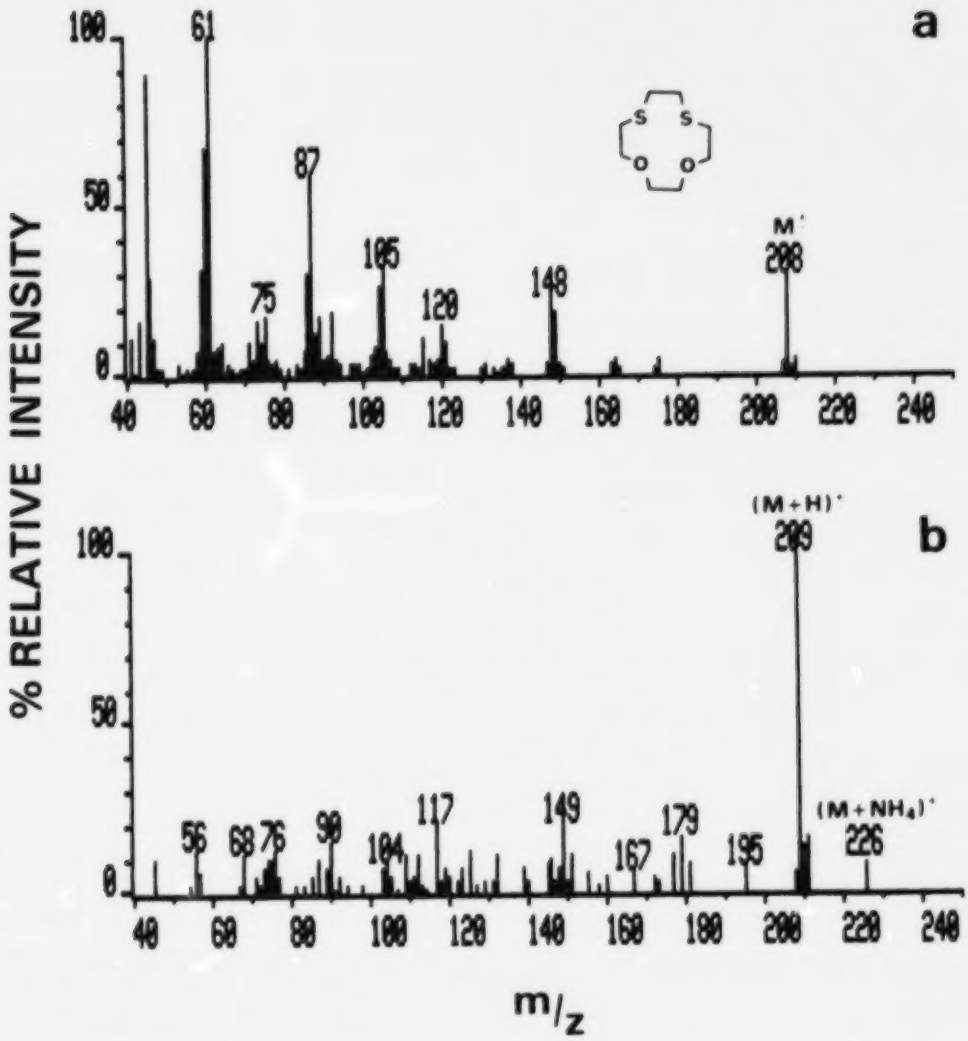


Figure 19

a) EI; and b) Ammonia CI Mass Spectra of 1,4-Dioxa-7,10-dithiacyclododecane (Peak Number 15)

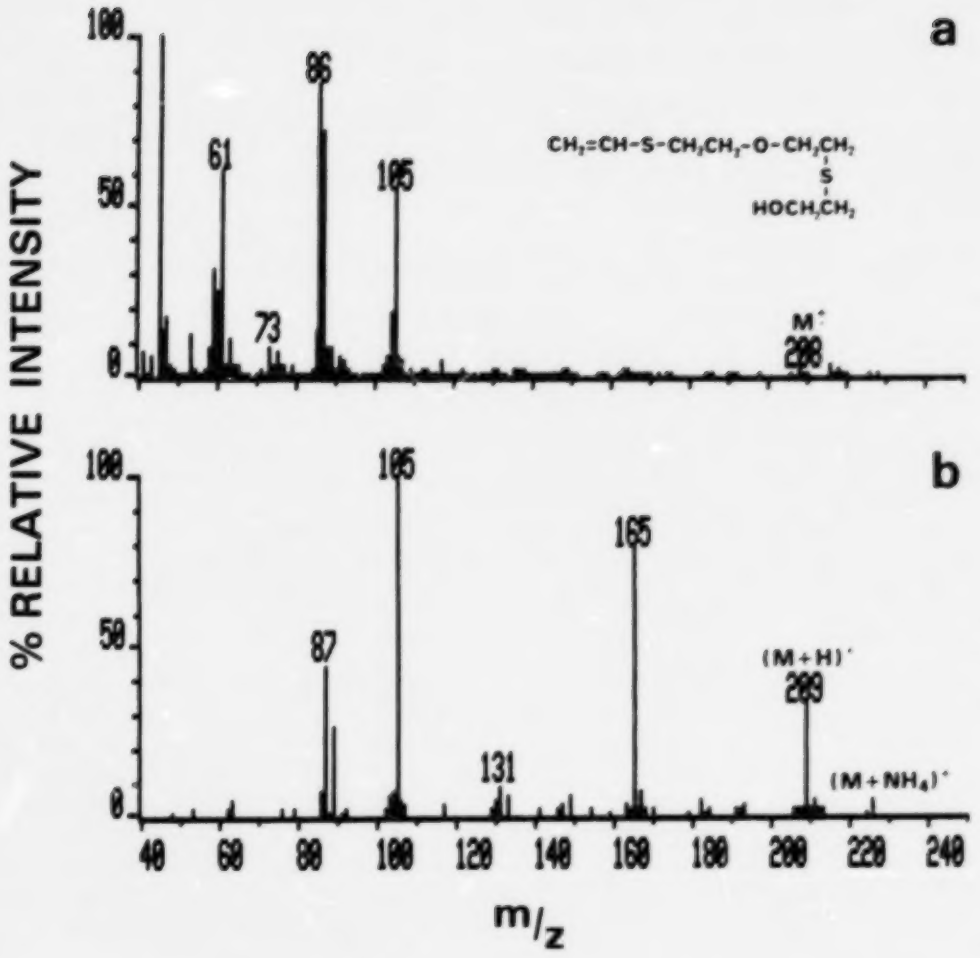


Figure 20

a) EI; and b) Ammonia CI Mass Spectra of (2-Hydroxyethylthio)ethyl (vinylthio)ethyl ether (Peak Number 16)

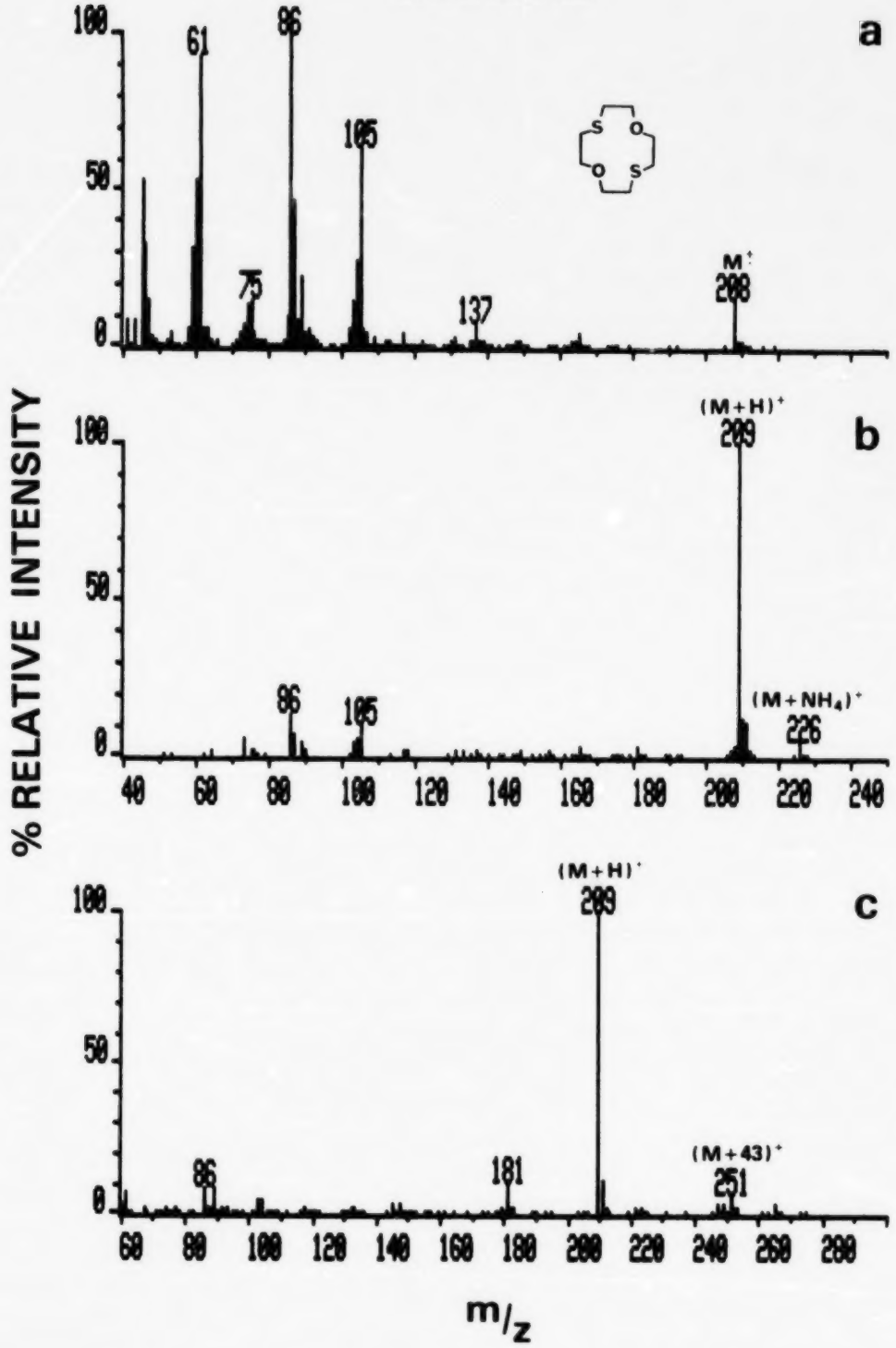


Figure 21

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of 1,7-Dioxa-4,10-dithiacyclododecane (Peak Number 17)

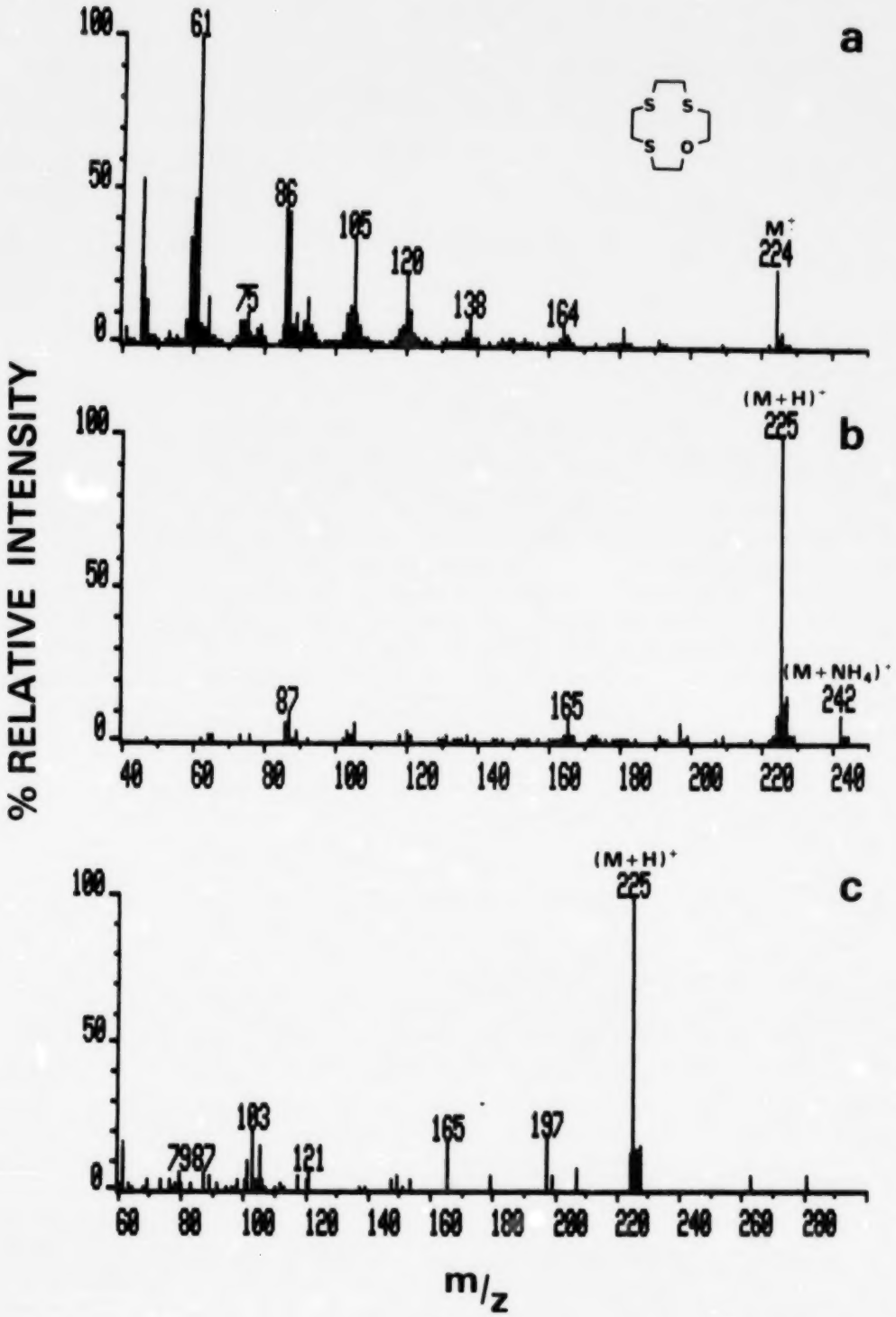


Figure 22

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of 1-Oxa-4,7,10-trithiacyclododecane (Peak Number 18)

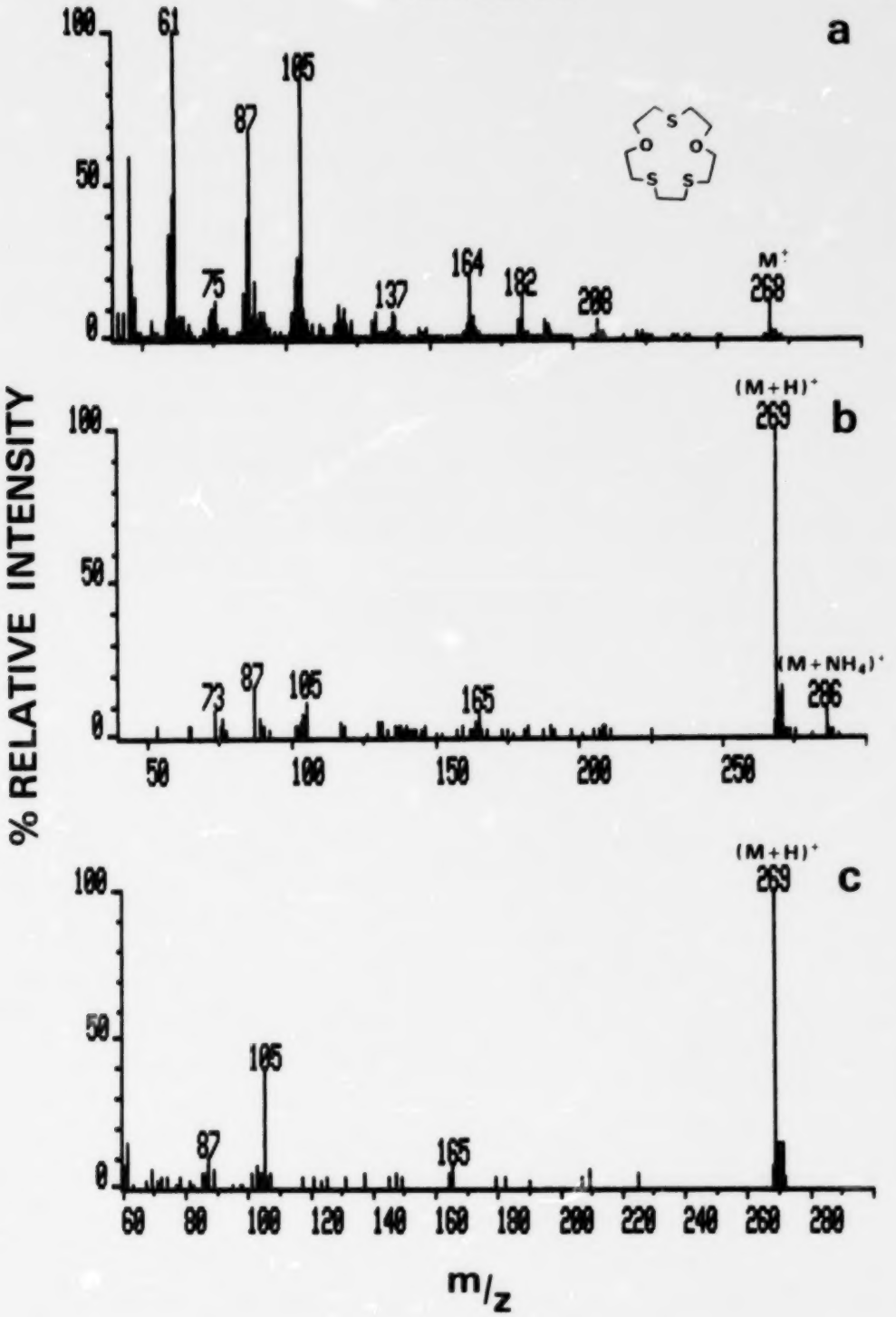


Figure 23

a) EI; b) Ammonia CI; and c) Isobutane CI Mass Spectra of 1,7-Dioxa-4,10,13-trithiacyclopentadecane (Peak Number 19)

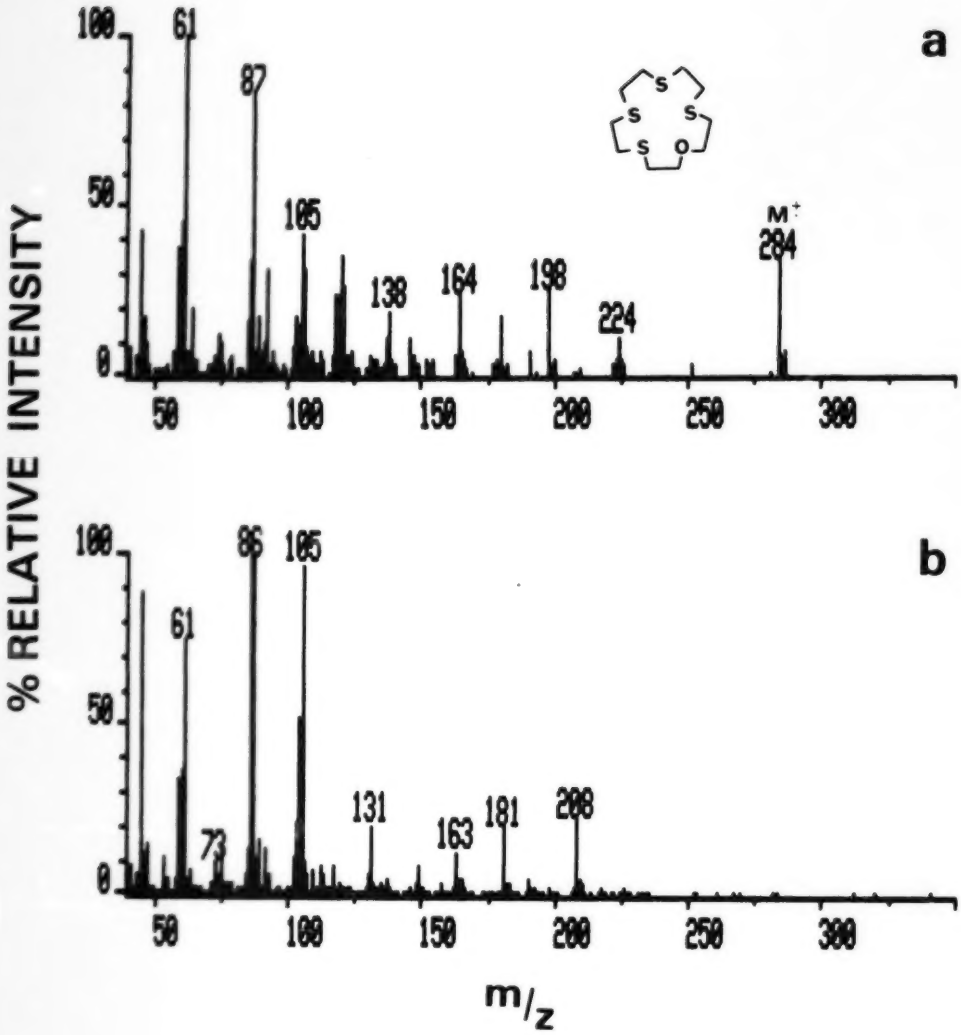


Figure 24

EI Mass Spectra of a) 1-Oxa-4,7,10,13-tetrathiacyclopentadecane; and b) an unknown (Peak Numbers 20 and 21)

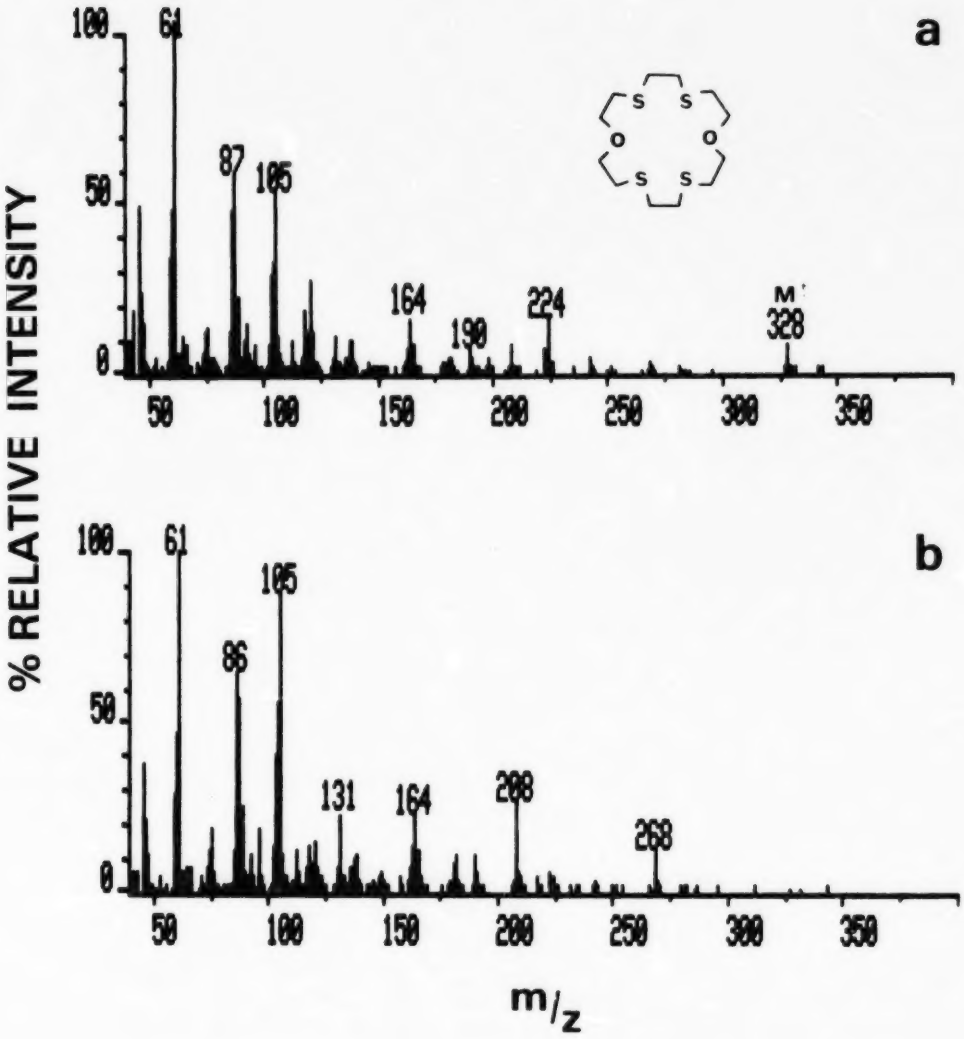


Figure 25

EI Mass Spectra of a) 1,10-Dioxa-4,7,13,16-tetrathiacyclooctadecane; and b) an unknown (Peak Numbers 23 and 24)

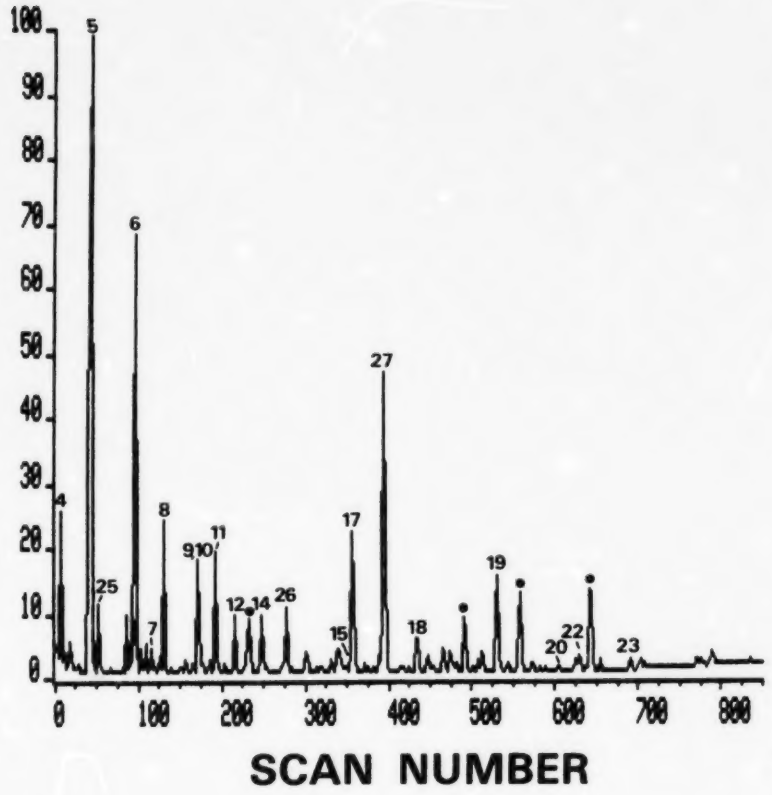


Figure 26

Capillary Column GC-MS (EI) Total-Ion-Current (600 to 40 u) of TMS Derivatized Hexane Extract of Ground Water Sample 87-5. (15 m × 0.32 mm ID J+W DB-1701; 40° (2 min) 10°/min 280°C (5 min); 1 MS scan = 1.6 sec). Numbered Peaks are Identified in Table II. (Peaks labelled with solid dot are derivatized unknowns.)

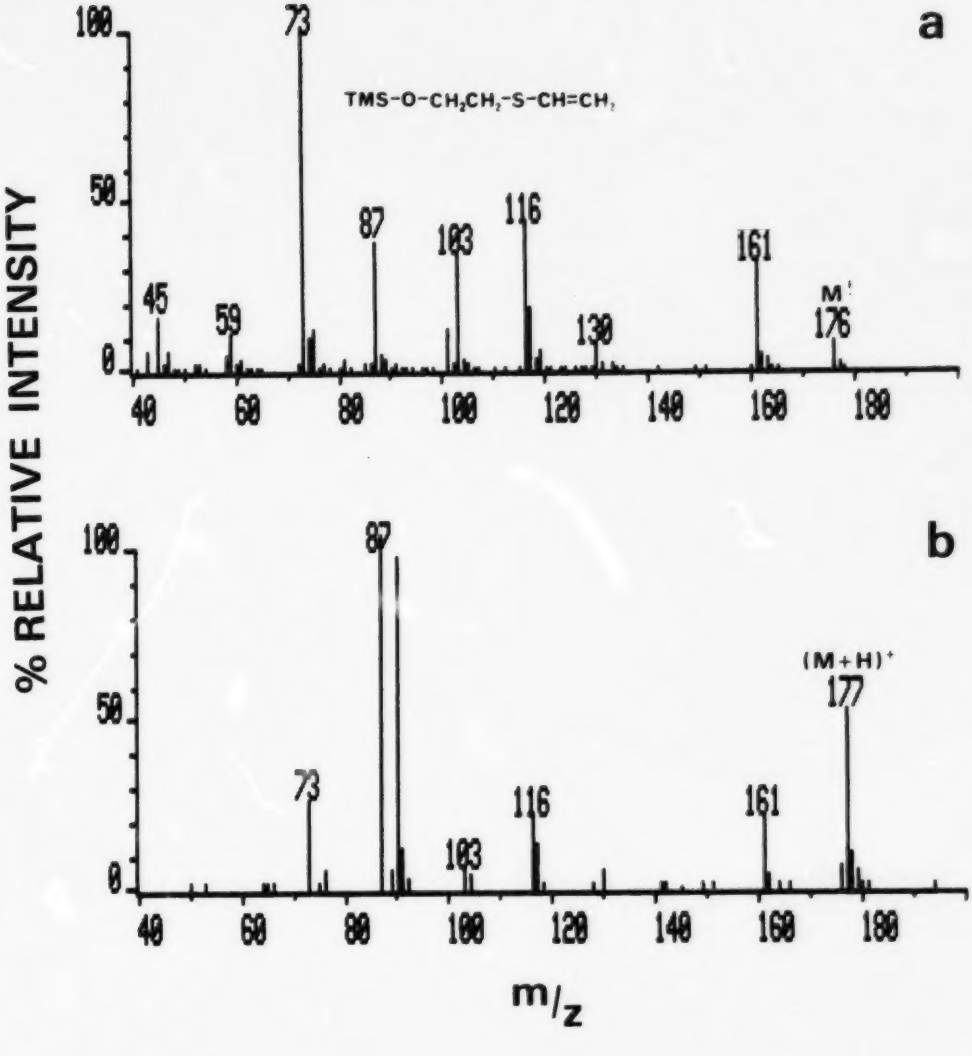


Figure 27

a) EI; and b) Ammonia CI Mass Spectra of TMS Derivative of (2-Vinylthio)ethanol (Peak Number 25)

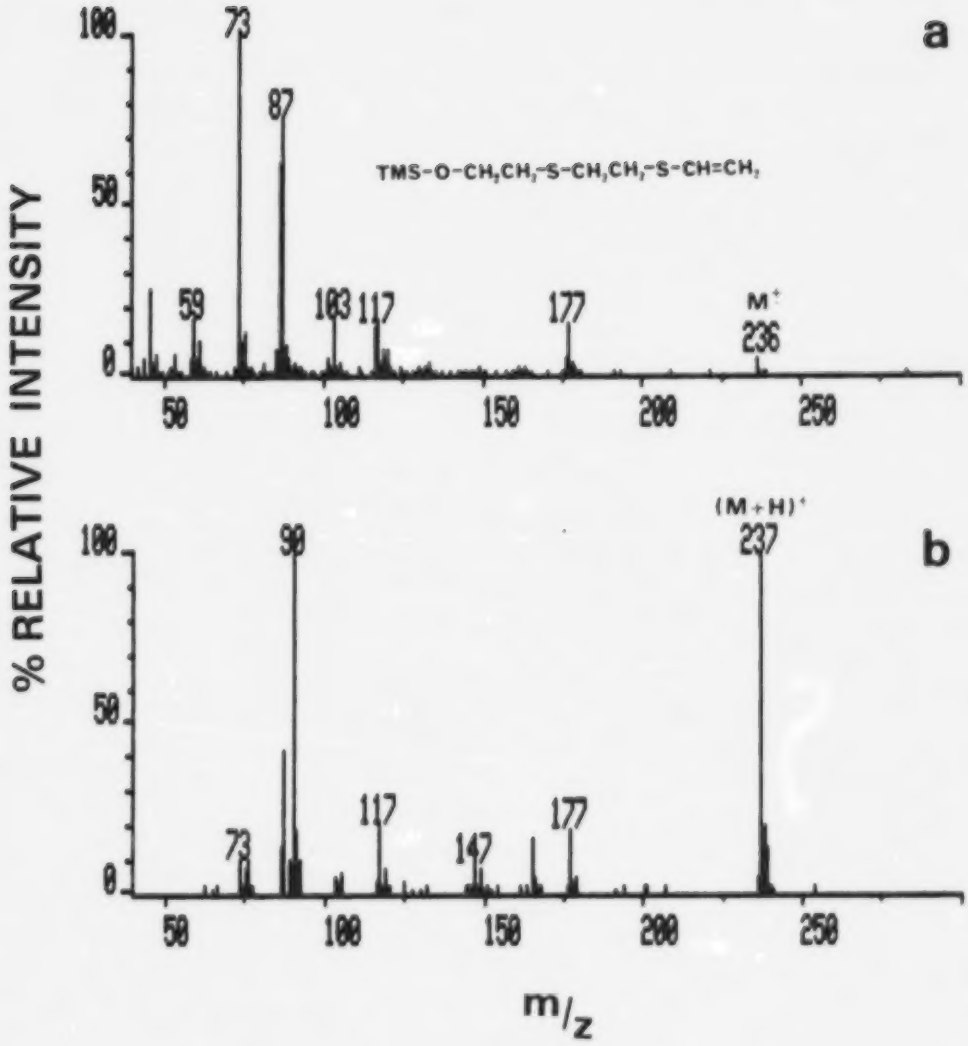


Figure 28

a) EI; and b) Ammonia CI Mass Spectra of TMS Derivative of (2-Hydroxyethylthio)ethyl vinyl sulfide (Peak Number 26)

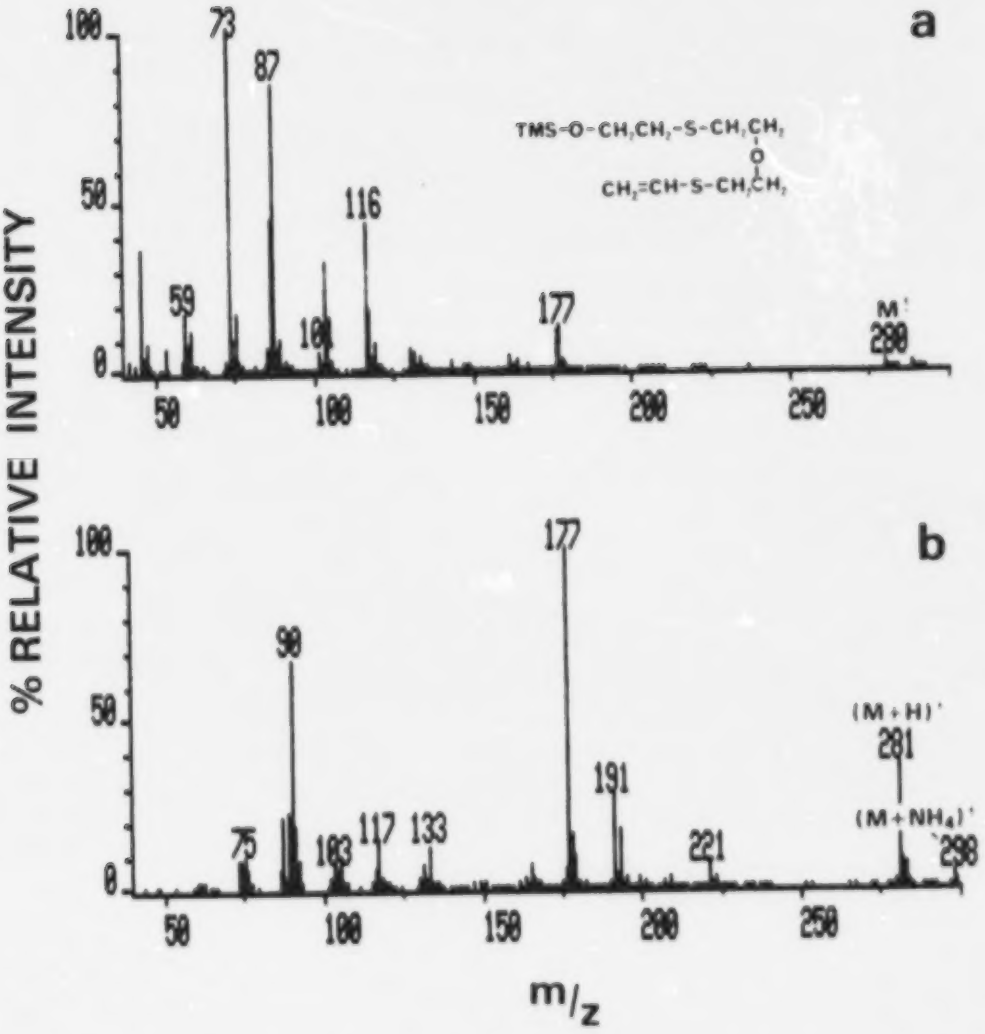


Figure 29

a) EI; and b) Ammonia CI Mass Spectra of TMS Derivative of (2-Hydroxyethylthio)ethyl (vinylthio)ethyl ether (Peak Number 27)

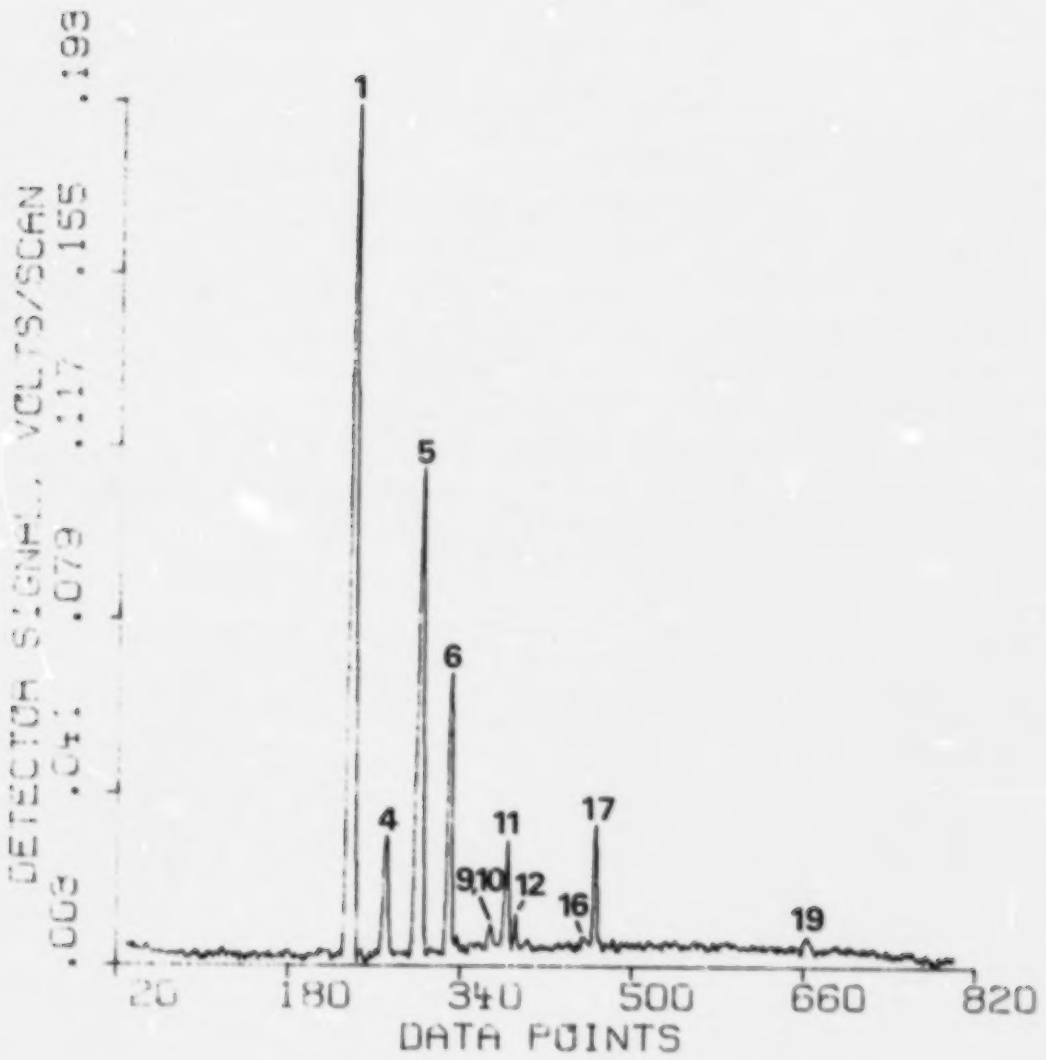


Figure 30

Capillary Column GC-FTIR Chromatogram of Hexane Extract of Ground Water Sample 84-5. (60 m × 0.32 mm ID J+W DB-5; 50°C 10°/min 280°C). Numbered Peaks are Identified in Table II.

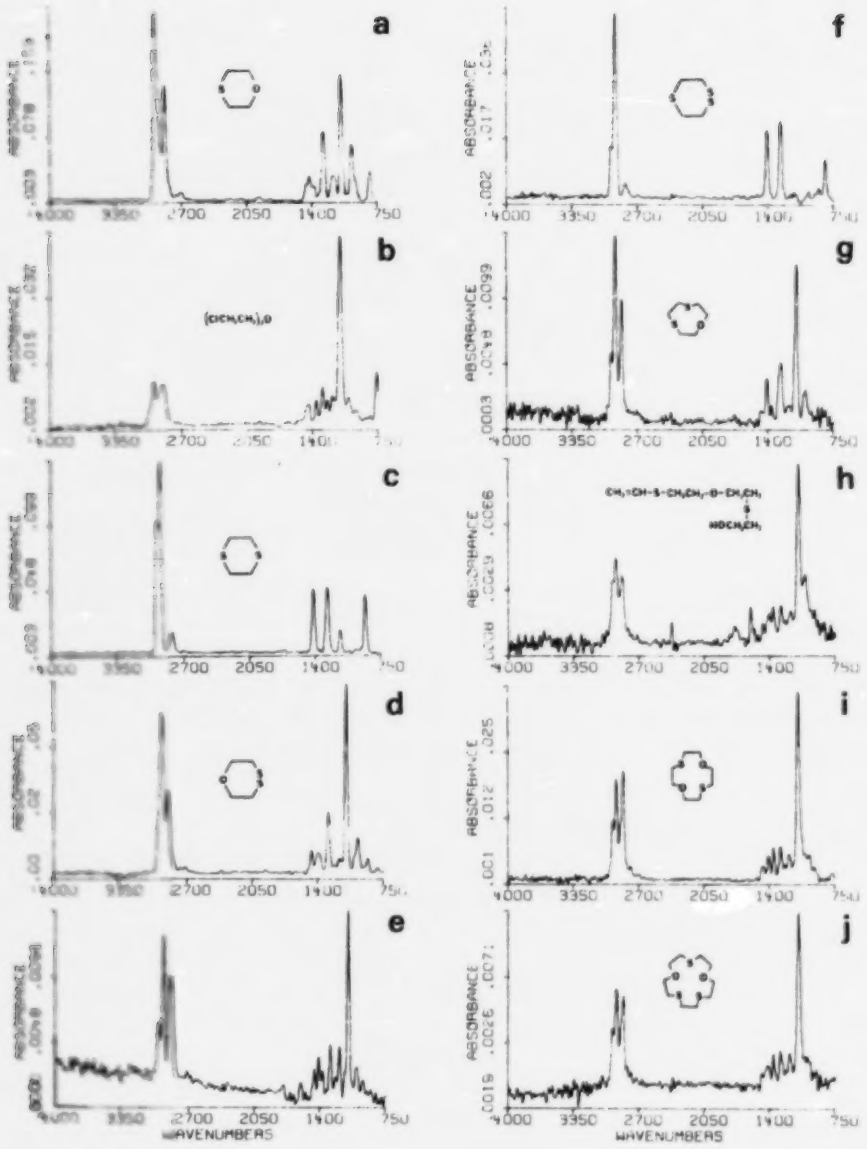


Figure 31

FTIR Data Obtained for Peak Numbers a) 1; b) 4; c) 5; d) 6; e) 9 and/or 10; f) 11; g) 12; h) 16; i) 17; and j) 19. (Compounds names are listed in Table II)

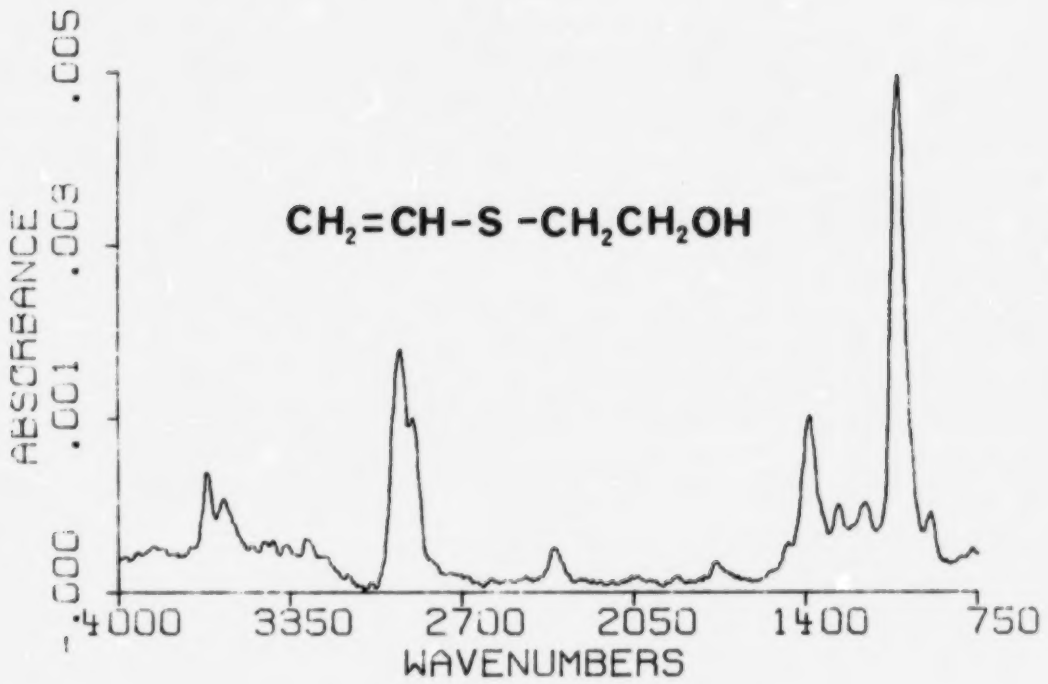


Figure 32

FTIR Spectrum of (2-Vinylthio)ethanol

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Thiodiglycol and a number of other compounds were detected during gas chromatographic analysis of aqueous samples obtained from near the site of the former DRES mustard hydrolysate vaults. Hexane extracts of the aqueous samples were analysed by capillary column gas chromatography-mass spectrometry (GC-MS) under both electron impact and chemical ionization conditions. Interpretation of the MS and complementary capillary column GC-fourier transform infrared data led to the characterization and identification of many compounds, including ether/thioether macrocycles and vinyl alcohol compounds, not previously associated with mustard decomposition.

KEY WORDS

Gas Chromatography
Mass Spectrometry
Chemical Ionization
Ammonia
Isobutane
Chemical Agent Detection
Military Chemical Agents
Mustard

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